THE PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS.

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1926.

THE PHYSICAL SOCIETY OF LONDON

1926-27.

PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY OF LONDON

SESSION 1925-1926.

Except where a statement to the contrary occurs, the meetings were held at the Imperial College of Science, the President being in the Chair.

October 23, 1925.

The following Papers were read :—

1. "The Influence of Strain on the Thomson Effect," by H. E. SMITH, B.Sc.

2. "The Measurement of Temperature by Thermocouples in Unequally Heated Enclosures," by W. MANDELL, B.Sc.

3. "On the Flashing of Certain Types of Argon-Nitrogen Discharge Tubes," by W. CLARKSON, M.Sc.

November 13, 1925.

Dr. W. H. ECCLES proposed and Dr. E. H. RAYNER seconded a vote of congratulation to Mr. F. E. SMITH on the recent presentation to him of the Hughes Medal of the Royal Society. The vote was carried by acclamation.

The following Papers were read :—

1. "On the Viscosity of Ammonia Gas," by R. G. EDWARDS, A.R.C.S., B.Sc., D.I.C., and B. WORSWICK, A.R.C.S., B.Sc., D.I.C.

2. "Valve Maintained Tuning Forks without Condensers," by T. G. HODGKINSON, A.M.I.E.E.

3. "The Times of Sudden Commencements of Magnetic Storms; Observation and Theory," by Dr. C. CHREE, F.R.S.

A DEMONSTRATION of "The Kinetic Properties of a Gas Jet" was given by Dr. . S. G. THOMAS.

November 27, 1925.

The following Papers were read :—

1. "Atomic Dimensions," by R. G. LUNNON.

2. "On Edge Tones" (I), by W. E. BENTON, B.Sc.

3. "The Spectroscopic Detection of Minute Quantities of Mercury," by J. J. MANLEY, M.A.

4. "On the Storage of Small Quantities of Gas at Low Pressures," by J. J. MANLEY, M.A.

A DEMONSTRATION of "An Instrument for Imitating the Eastward Deviation of Bodies Falling from a Great Height" was given by Mr. G. R. MATHER.

December 11, 1925.

The following Papers were read :—

1. "The Effect of Rolling on the Crystal Structure of Aluminium," by E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A.

2. "On the Spreading of One Liquid on the Surface of Another," by R. S. BURDON, B.Sc., A.Inst.P.

3. "On the Advance of the Perihelion of Mercury," by J. T. COMBRIDGE, M.A., M.Sc.

January 5, 6 and 7, 1926.

The Annual Exhibition of Apparatus was held by the Physical Society of London and the Optical Society from 3-6 p.m. and from 7-10 p.m. each day.

Discourses were given as follows :—

At 8 p.m., January 5, "The Search for Ultra-Microscopic Organisms," by J. E. BARNARD, F.R.S.

At 8 p.m., January 6, "The Mechanical Design of Instruments," by Prof. A. F. C. POLLARD, A.R.C.S., A.M.I.E.E.

At 8 p.m., January 7, "Electrical Listening," by Major W. S. TUCKER, D.Sc.

January 22, 1926.

The following Papers were read :—

1. "A Critical Discussion of the Determinations of the Mechanical Equivalent of Heat," by Prof. T. H. LABY, M.A., Sc.D., F.Inst.P.

2. "The Present Status of Theory and Experiment relating to Specific Heats and the Chemical Constant," by F. IAN G. RAWLINS, B.A.

After the first Paper Prof. LABY gave an account of experiments made by himself and Mr. E. D. HERCUS on a direct determination of the Mechanical Equivalent of Heat.

February 12, 1926.

Annual General Meeting.

GENERAL BUSINESS.

The Report of the Council and that of the Treasurer were presented and unanimously adopted.

REPORT OF THE COUNCIL.

During the year fourteen ordinary Science Meetings have been held at the Imperial College of Science. In addition, by kind invitation of Prof. F. A. Lindemann, about 180 Fellows of the Society and their friends visited Oxford on July 4. Prof. Lindemann entertained the visitors to lunch in Christ Church Hall and to tea in Wadham College Hall. The Clarendon Laboratory was open for inspection, and a Science Meeting was held there after tea, when several Papers were read by workers in the Laboratory.

At the Science Meetings held during the year 38 Papers were presented and 12 Demonstrations were given.

Mr. F. E. Smith gave his Presidential Address on February 13. The subject was "A System of Electrical Measurements," and the address was illustrated by experiments.

Prof. Willy Wien, of Munich, delivered on April 24 the Tenth Guthrie Lecture on "Recent Researches in Positive Rays." About 130 Fellows and visitors were present.

On May 22 Prof. L. S. Ornstein, of Utrecht, gave a lecture to the Society on "The Intensity of Spectral Lines: Measurement and Theory."

The average attendance at the meetings of the Society was 64.

The Fifteenth Annual Exhibition of Scientific Apparatus, arranged jointly by the Physical and Optical Societies, was held, through the courtesy of the Governing Body, at the Imperial College, on January 7 and 8. Exhibits were arranged by sixty firms, and the attendance was large, probably about 3,000. Discourses were given by

Mr. F. Twyman on "Some Experiments with Interferometers," and by Mr. C. F. Elwell on "Talking Motion Pictures."

Arrangements have been made for the extension of the scope of future Exhibitions by the inclusion, in addition to the ordinary trade exhibits, of new groups illustrating the results of recent physical research and improvements in laboratory practice, lecture experiments, and famous historical experiments in physics. The Exhibition will remain open for a third day, on which the general public will be admitted. These changes take effect in January, 1926.

Dr. D. Owen and Dr. J. H. Vincent have been appointed representatives of the Society on the Board of the Institute of Physics, and Mr. T. Smith and Dr. D. Owen on the Science Abstracts Committee. Mr. F. J. W. Whipple has been re-appointed as the Society's representative on the Geophysical Committee of the Royal Astronomical Society.

At the invitation of the National Institute for the Blind, the Council has nominated Dr. W. S. Tucker as a member of the Technical and Research Committee of the Institute.

Dr. C. E. Guillaume, Honorary Fellow, acted as delegate of the Society at the International Conference on the use of Esperanto, in Paris, May 14-16; and Dr. E. A. Owen was the official representative of the Society at the International Congress on Radiology in London, July 1-4.

Messages of congratulation have been sent to the Russian Academy of Science on the attainment of its bicentenary, and to Prof. H. A. Lorentz, the senior Honorary Fellow of the Society, on the occasion of his Doctorate Jubilee.

The numerous copies of the Proceedings of the Society which came into its possession through the kindness of Lady Thorpe have been presented to the Library of the University College of North Wales, Bangor. The Council also presented a bound copy of Wheatstone's Papers to the Gloucester Public Library on the occasion of the unveiling of the Wheatstone Memorial.

The Council has awarded the Third Duddell Medal to Mr. Albert Campbell. This medal will be presented at the Annual General Meeting.

Negotiations with the Institution of Electrical Engineers for a new agreement in relation to Science Abstracts have been carried on, and are nearly complete.

The Council has appointed a sub-committee to inquire into the desirability of changing the name of the Society, and now has the report of the sub-committee under consideration.

Through the courtesy of the Governing Body, it has been possible to resume the use of the original room in the Imperial College for the purposes of the business of the Society.

The Society has to record with regret the deaths of Prof. A. Liveing, Prof. Sir Edward Thorpe, Sir William Barrett, Dr. E. Hopkinson, Prof. E. H. Barton and Mr. H. St. G. Anson. Sir William Barrett was one of the few remaining Original Fellows,

and took a prominent part in founding the Society. He was a Life Fellow. Prof. Liveing, Dr. Hopkinson and Sir Edward Thorpe were also Life Fellows of long standing, having been elected in 1879, 1882 and 1885 respectively. Prof. Barton was elected in 1892, and had served on the Council and as Vice-President ; Mr. St. G. Anson was one of the youngest Fellows ; he was elected in 1923.

The number of Honorary Fellows on the Roll on December 31, 1925, shows an increase to 11, Prof. Willy Wien having been added at the last Annual General Meeting. The number of Ordinary Fellows and Students at the same date stands at 656 (Fellows 640, Students 16). During the year 55 new Fellows were elected, 10 being transfers from Student Membership, and nine Students were admitted.

Report of the Treasurer.

The financial position of the Society may be considered as satisfactory, the Income having exceeded the Expenditure.

The Council is indebted to the Council of the Royal Society for a grant of £100 towards the cost of publications. It has also to acknowledge the generous attitude adopted by the Institution of Electrical Engineers towards the cost of the publication of "Science Abstracts" for 1924.

The Council has decided that in future the Entrance Fees received from Fellows shall not be treated as Income, but shall be invested in the same way as the Life Composition Fees. The Entrance Fees received during the past year have therefore been placed to the Accumulated Fund.

£150 Southern Railway 5 per cent. Debenture Stock was purchased, this amount approximately covering the Composition Fees of Fellows elected during 1924 and 1925.

The investments have been valued at market prices through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank. Owing to the fall in value of securities during the year, the market value of the Society's investments (including the Trust Funds) decreased during the twelve months by £195 15s. 5d.

Discussion of the Reports,

The retiring President, inviting a general discussion on the reports, said that he hoped the new Council would continue to arrange visits to centres of learning other than London from time to time. The meetings held by the Society at Oxford in 1925, and Cambridge in 1924, had been most successful.

Dr. Lewis Simons reminded the President that the latter had once put forward a proposal that the Societies concerned in Physics should combine to provide a joint home of their own. The financial difficulties would be very great, but he felt that the proposal should not be lost sight of.

Sir Richard Paget inquired what the cost of such a scheme would be.

Dr. C. Chree said that the Royal Meteorological Society had found that the cost of a suitable building in Kensington was about £6,000.

INCOME AND EXPENDITURE ACCOUNT.

From January 1st to December 31st, 1925.

1924. £ s. d.	Expenditure.	£ s. d.	£ s. d.
	"Science Abstracts," 1925 (Inst. El. Eng.)	417 0 0	
	Ditto, 1924 (balance)	96 0 0	
281 0 0			513 0 0
	Ordinary Publications :—		
786 14 2	"Proceedings"	892 1 1	
63 11 5	"Bulletin"	70 5 0	
102 14 2	General	102 8 7	
			1,064 14 8
87 6 2	Postage of Publications		93 1 2
61 14 4	Reporting	62 1 1	
26 19 4	Refreshments and Expenses of Ordinary Meetings	29 6 3	
181 11 0	Expenses of Exhibition held jointly with the Optical Society	203 14 0	
28 8 10	Secretary's Expenses	17 11 4	
18 14 1	Treasurer's Expenses	10 9 6	
7 15 0	Periodicals and Library	8 5 1	
1 15 0	Insurance	1 15 0	
2 2 0	Registered Address	2 2 0	
0 10 6	Cheque Books	0 5 2	
4 12 0	Advertising.		
15 12 0	Accountancy Charges and Clerical Assistance	20 15 0	
	Sundry Expenses	2 15 9	
			359 0 2
10 0 0	Guthrie Lecture (Honorarium)	20 0 0	
	Donation to 1926 Optical Convention	10 10 0	
	Donation to Lorentz Memorial	5 5 0	
			35 15 0
20 0 0	Donation to Institute of Physics.		
25 0 0	Grant to the Widow of A. V. Parke.		
277 12 8	Excess of Income over Expenditure		90 7 1
£2,003 15 8			£2,155 18 1

1924. £ s. d.	Income.	£ s. d.	£ s. d.
866 5 8	Subscriptions by Fellows*	954 0 10	
9 9 0	" Voluntary†	9 9 0	
8 18 6	" by Students	8 18 6	
10 10 0	Institute of Physics.		
4 12 6	Arrears.		
36 0 0	Subscriptions for "Science Abstracts" and Advance Proofs	42 11 0	
935 15 8			1,014 19 4
639 17 7	Sale of Publications (Fleetway Press, Ltd.)		605 6 10
	Dividends :—		
43 7 4	London Midland & Scottish Railway	43 14 4	
7 0 0	Metropolitan Board of Works	7 0 0	
9 6 0	Lancaster Corporation Stock	9 9 0	
14 4 11	New South Wales Stock	10 0 2	
23 9 5	Southern Railway	23 15 1	
15 10 0	London & North Eastern Railway	15 12 6	
17 10 0	India 3½%	17 10 0	
20 3 0	4% Funding Loan	20 9 6	
35 0 0	5% War Loan	35 0 0	
1,761 3 11		182 10 7	
20 0 0	*Less :* Transferred to Duddell Memorial Trust Fund	20 0 0	
1,741 3 11			162 10 7
58 17 3	Income Tax repayable one year to December 31, 1925		40 0 0
5 5 4	Interest on Deposit Account		9 19 8
8 6 8	Optical Society for Share of Exhibition Expenses		4 5 10
138 18 6	Exhibitors' Payments on account of Exhibition Catalogues		193 2 6
	Royal Society Grant for Publications		100 0 0
	Royal Meteorological Society for Share in the cost of the Publication of the Discussion on "Ionization of the Atmosphere, etc."		25 13 4
5 0 0	Translating Dr. Jeans' Report.		
46 4 0	Entrance Fees.		
£2,003 15 8			£2,155 18 1

ROBERT S. WHIPPLE, *Honorary Treasurer.*

Audited and found correct,

T. MATHER
R. L. SMITH-ROSE } *Honorary Auditors.*

January 27th, 1926.

Liabilities.	£ s. d.	£ s. d.
Accumulated Fund:—		
Balance as per last account	1,880 5 4	
Entrance Fees, 1925	31 10 0	
	1,911 15 4	
Less Decreased Value of Investments	165 15 5	
	1,745 19 11	
Add Excess of Income over Expenditure, 1925...	90 7 1	
		1,836 7 0
Life Compositions:—		
Balance as per last Account	2,154 0 0	
Added during year	51 10 0	
		2,205 10 0
Duddell Memorial Trust Fund as per last Account	432 12 9	
Less Decreased Value of Investments	4 0 0	
		428 12 9
W. F. Stanley Trust Fund as per last Account...	449 0 0	
Less Decreased Value of Investments	26 0 0	
		423 0 0
Sundry Creditors		529 17 1
Subscriptions paid in advance		21 0 0
		£5,444 6 10

Assets.	£ s. d.	£ s. d.
Investments at Market Value on date:—		
£399 London Midland & Scottish Railway 4 per cent. Debenture Stock	323 0 0	
£1,000 London Midland and Scottish Railway 4 per cent. Preference Stock	735 0 0	
£200 Metropolitan Board of Works 3½ per cent. Stock	188 0 0	
£400 Lancaster Corporation 3 per cent. Redeemable Stock	280 0 0	
£254 2s. 9d. New South Wales 5 per cent. 1935-55	252 0 0	
£300 Southern Railway Preferred Ordinary Stock	228 0 0	
£442 Southern Railway Deferred Ordinary Stock	195 0 0	
£150 Southern Railway 5 per cent. Debenture Stock	149 0 0	
£500 London & North Eastern Railway 4 per cent. Debenture Stock	380 0 0	
£500 India 3½ per cent. Stock	332 0 0	
£650 4% Funding Loan, 1960-90	558 0 0	
£300 5% War Loan 1929/47 inscribed, "A" Account	301 0 0	
£400 5% War Loan 1929/47 inscribed, "B" Account (Duddell Memorial Fund)	402 0 0	
		4,323 0 0
Stock of Publications (as per Treasurer's valuation)		400 0 0
Subscriptions due	29 1 9	
Due from Fleetway Press (Contra)	177 10 0	
Due from Customs and Excise for Income Tax Reclaim	32 4 2	
		238 15 11
Cash at Bankers, Deposit Account	300 0 0	
Cash at Bankers, Current Account	171 12 7	
Cash in hand of Treasurer	9 13 0	
Petty Cash in hand	1 5 4	
		482 10 11
		£5,444 6 10

Audited and found correct,

ROBERT S. WHIPPLE, *Honorary Treasurer.*

January 27th, 1926.

T. MATHER
R. L. SMITH-ROSE } *Honorary Auditors.*

Note.—The value of the Society's library has not been brought into the Balance Sheet.

LIFE COMPOSITION FUND AT DECEMBER 31ST, 1925.

	£	s.	d.
128 Fellows paid £10	1,280	0	0
3 Fellows paid £15	45	0	0
1 Fellow paid £20	20	0	0
1 Fellow paid £20 10s.	20	10	0
13 Fellows paid £21	273	0	0
18 Fellows paid £31 10s.	567	0	0
164	£2,205	10	0

W. F. STANLEY TRUST FUND (FOR THE "BULLETIN").

	£	s.	d.		£	s.	d.
£300 Southern Railway Preferred Ordinary Stock	228	0	0	Carried to Balance Sheet	423	0	0
£442 Southern Railway Deferred Ordinary Stock	195	0	0				
	£423	0	0		£423	0	0

DUDDELL MEMORIAL TRUST FUND.

CAPITAL.

	£	s.	d.		£	s.	d.
£400 War Loan 5% 1929/47 inscribed Stock	402	0	0	Carried to Balance Sheet	402	0	0

REVENUE.

	£	s.	d.		£	s.	d.
Balance at 31st December, 1924	26	12	9	Honorarium to Medallist	20	0	0
Dividends	20	0	0	Balance carried to Balance Sheet	26	12	9
	£46	12	9		£46	12	9

Audited and found correct,

T. MATHER
R. L. SMITH-ROSE } *Honorary Auditors.*

ROBERT S. WHIPPLE, *Honorary Treasurer.*

January 27th, 1926.

ELECTION OF OFFICERS AND COUNCIL.

The following Officers and Members of Council were elected for the year 1926-1927:—

President.—Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President).—Sir Oliver J. Lodge, D.Sc., F.R.S.; Sir Richard Glazebrook, K.C.B., D.Sc., F.R.S.; C. Chree, Sc.D., LL.D., F.R.S.; Prof. H. L. Callendar, M.A., LL.D., F.R.S.; Sir Arthur Schuster, Ph.D., Sc.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.; Prof. C. Vernon Boys, F.R.S.; Prof. C. H. Lees, D.Sc., F.R.S.; Prof. Sir W. H. Bragg, K.B.E., M.A., F.R.S.; Alexander Russell, M.A., D.Sc., F.R.S.; F. E. Smith, C.B.E., F.R.S.

Vice-Presidents.—E. H. Rayner, M.A., Sc.D.; J. H. Vincent, D.Sc., M.A.; D. Owen, B.A., D.Sc.; Prof. F. L. Hopwood, D.Sc.

Hon. Secretaries.—Prof. A. O. Rankine, O.B.E., D.Sc., Imperial College of Science and Technology; J, Guild, A.R.C.S., D.I.C., National Physical Laboratory, Teddington, Middlesex.

Hon. Foreign Secretary.—Sir Arthur Schuster, Ph.D., Sc.D., F.R.S.

Hon. Treasurer.—R. S. Whipple, 45, Grosvenor Place, S.W.1.

Hon. Librarian.—J. H. Brinkworth, M.Sc., A.R.C.S., Imperial College of Science and Technology.

Other Members of Council.—R. W. Paul; Prof. A. M. Tyndall, D.Sc.; W. S. Tucker, D.Sc.; A. Ferguson, M.A., D.Sc.; J. S. G. Thomas, D.Sc.; D. W. Dye, B.Sc.; Sir Richard Paget, Bart.; E. A. Owen, B.A., D.Sc.; J. Robinson, M.Sc., Ph.D.; A. B. Wood, D.Sc.

PRESENTATION OF THE DUDDELL MEDAL.

The PRESIDENT, on behalf of the Council, presented the Duddell Memorial Medal to Albert Campbell, B.A.

After repeating the conditions governing the award, the PRESIDENT said that the medallist's name had been known for a quarter of a century to all who are interested in the design of instruments. He had enriched scientific apparatus with many beautiful devices, and knew Duddell intimately. The speaker, looking back on 20 years' acquaintance with Mr. Campbell as a colleague, attributed his success to his wide scientific knowledge, to his manipulative skill, and to his patience. He had always been generous in his appreciation of others' achievements.

Mr. CAMPBELL, after expressing his thanks, said that the design of instruments involves invention rather than discovery. He thought that in addition to the qualifications which the President had mentioned, the inventor or designer should have a high degree of *distractibility*. He should set his face against conventional methods, and be ready to abandon any line of thought upon which he might be engaged for a new

one if this should occur to him. "Scientific wool-gathering" was characteristic of Lord Kelvin.

ELECTION OF AN HONORARY FELLOW.

Prof. CHARLES FABRY was elected an Honorary Fellow of the Society.

VOTES OF THANKS.

A vote of thanks to the Hon. Auditors was proposed by Mr. C. R. Darling, seconded by Dr. J. H. Vincent, and carried by acclamation.

A vote of thanks to the retiring Officers and Council was moved by Mr. T. Smith, seconded by Mr. Rollo Appleyard, and carried by acclamation. Particular reference was made to Prof. Rankine's services in organizing the Annual Exhibition of Apparatus, and to the debt which the Society owes to the retiring President.

A vote of thanks to the Governors of the Imperial College of Science was proposed by Dr. D. Owen, seconded by Prof. F. L. Hopwood, and carried by acclamation. Dr. Owen said that some reference had been made to the Society's need for a home of its own, but he felt that it had been made to feel very much at home in the College.

ORDINARY MEETING FOLLOWING THE ANNUAL GENERAL MEETING.

The following Papers were read :—

1. "On the Hyperbola Method for the Measurement of Surface Tension," by A. FERGUSON, M.A., D.Sc., and I. VOGEL, B.Sc.

2. "The Application of Radiography to the Study of Capillarity," by E. A. OWEN, M.A., D.Sc., and A. F. DUFTON, M.A., D.I.C.

A DEMONSTRATION of "The Application of the Piezo-Electric Properties of a Rochelle Salt Crystal and the Tri-Electrode Valve to the Determination of Impact Stresses in Granular Material" was given by J. J. HARTLEY, M.Eng.M.Sc., A.M.I.C.E., and R. H. RINALDI.

February 26, 1926.

The following Papers were read :—

1. "The Effects of Torsion upon the Thermal and Electrical Conductivities of Aluminium, with special reference to Single Crystals," by J. E. CALTHROP, M.A., M.Sc., East London College.

2. "A Study of the Concurrent Variations in the Thermionic and Photo-electric Emission from Platinum and Tungsten with the State of the Surfaces of these Metals," by T. H. HARRISON B.Sc., King's College, London.

DEMONSTRATIONS of Some Phenomena of Surface Tension were given by Mr. EDWIN EDSER and by Mr. CHARLES R. DARLING, F.I.C.

March 12, 1926.

The following Papers were read :—

1. "The Analogy between Ripples and Acoustical Wave Phenomena," by A. H. DAVIS, D.Sc.

2. "On the Evaporative Losses of Vacuum-Jacketed Metal Vessels of the Dewar Type," by R. M. ARCHER, A.R.C.Sc., B.Sc., M.I.E.E.

The first of the above Papers was illustrated by a Demonstration.

March 26, 1926.

The PRESIDENT announced that the Council had passed the following resolution with regard to the death of Mr. W. R. Cooper, and that three officers of the Society had been able to attend Mr. Cooper's funeral.

RESOLUTION.

By the death of Mr. W. R. Cooper the Physical Society of London has lost one of its devoted friends, and the Council wishes to express to Mrs. Cooper and family its deep sympathy in their loss.

Mr. Cooper acted as a Member of the Council from February 8, 1901, until February, 1903, when he became one of the Secretaries of the Society. He continued in this office until February 12, 1915, when he was elected a Vice-President. He resigned this position in February, 1918, to accept the responsibilities of Treasurer, and acted in this capacity until his breakdown in October, 1924. He was thus continuously in office for more than 23 years.

It was largely due to his efforts, in conjunction with the late Mr. W. Duddell, that the "Proceedings" were published separately from the "Philosophical Magazine." By taking this step the Society was enabled to publish its Papers more efficiently and with considerable financial advantage.

He was a most careful Treasurer, and the Society is largely indebted for its present financial position to his devotion.

The Council will much miss his good judgment, and the Fellows his lovable personality.

Mr. F. E. SMITH moved that the meeting should associate itself with the Council's resolution. The Fellows present signified their assent by standing.

The following Papers were read :—

1. "Obliquity Corrections in Radium Estimation," by I. BACKHURST, M.Sc.

2. "The Viscosity of Water at Low Rates of Flow, determined comparatively by a Method of Thermal Convection," by Prof. A. GRIFFITHS, D.Sc., A.R.C.S., and P. C. VINCENT, B.Sc., Birkbeck College.

A DEMONSTRATION of some Simple Experiments with Thermionic Valves was given by E. H. RAYNER, M.A., Sc.D.

April 23, 1926.

The Eleventh Guthrie Lecture was delivered by Prof. CHARLES FABRY, who took as his subject "The Absorption of Radiation by the Upper Atmosphere."

A vote of thanks, proposed by Sir ARTHUR SCHUSTER and seconded by Mr. J. H. JEANS, was carried by acclamation.

May 14, 1926.

The following Papers were read :—

1. "The Properties of Mutual Inductance Standards at Telephonic Frequencies," by L. HARTSHORN, A.R.C.S., B.Sc., D.I.C.

2. "A Note on λ 4722 of Bismuth and the Nature of '*raies ultimes*,'" by Prof. A. L. NARAYAN, and K. R. RAO.

3. "The Distribution of Intensity in a Positive Ray Spectral Line," by M. C. JOHNSON, M.A., M.Sc.

A DEMONSTRATION of "Some Experiments with Selenium Cells" was given by Dr. E. E. FOURNIER D'ALBE.

May 28, 1926.

The following Papers were read :—

1. "Static and Isotropic Gravitational Fields," by G. TEMPLE, Ph.D.

2. "On The Diffraction of Light by Spherical Obstacles," by Prof. C. V. RAMAN, F.R.S., and K. S. KRISHNAN.

3. "On the Absorption and Series Spectra of Nickel," by Prof. A. L. NARAYAN and K. R. RAO.

4. "The Influence of Electrolytes in Electro-Endosmosis," by H. C. HEPBURN, B.Sc.

June 11, 1926.

The following Papers were read :—

1. "The Latent Heat of Fusion of Some Metals," by J. H. AWBERY, B.Sc., and EZER GRIFFITHS, D.Sc.

2. "The Piezo-Electric Quartz Resonator and its Equivalent Electric Circuit," by D. W. DYE, B.Sc.

3. "The Characteristics of Electrostatic Machines on Non-Inductive Loads and on the Coolidge Tube," by E. J. EVANS.

June 25, 1926.

The following Papers were read :—

1. "The Refraction and Dispersion of Gaseous Carbon Disulphide," by H. LOWERY, M.Sc.

2. "On the Use of Invar Steel for Precision Balances," by J. J. MANLEY, M.A.

3. "On the Scattering Power of Oxygen and Iron for X-Rays," by A. A. CLAASSEN.

XXXIII.—STATIC AND ISOTROPIC GRAVITATIONAL FIELDS.

By G. TEMPLE, *Ph.D.*, Imperial College of Science.

Received March 8, 1926.

¶1. ABSTRACT.

The object of this Paper is to give a brief account of the principles of Einstein's General Theory of Relativity as applied to those problems in which they have received their most striking confirmation. To this end we have limited our investigations to the consideration of dynamical manifolds which are static and isotropic in character. It has then proved possible to abandon the notation and theory of the Absolute Differential Calculus, and to substitute in its place some classical theorems of Lord Kelvin and M. J. Liouville. Although the scope of these inquiries is not extensive, within the limits of our investigations we have explained the method of the construction and solution of Einstein's field equations, and have given the applications of these results to the problems of planetary motion and of the deviation of light rays in the solar gravitational field. At the same time we have endeavoured to make explicit the various assumptions involved in this theory.

I. THE LAWS OF MOTION.

¶2. *Particle Geodesics.*

THE first assumption which we make refers to the form in which we shall enunciate the law of motion of a mass-particle. The motion of a particle will be completely specified by the path which it describes together with the speed with which the path is traversed ; and the complex of the spatial and temporal relations which are involved in this specification will be called the " route " of the particle. To determine the actual route pursued by a particle which is known to pass through the points A_1 and A_2 at times t_1 and t_2, we consider the qualifications of all possible routes which possess these fixed termini. With each possible route we associate an integral J, called, in Whitehead's terminology, the " realised impetus " of the route. Then we determine that route which possesses the two termini fixed above and which renders the impetus stationary, in the sense of the calculus of variations.

It is not an unreasonable assumption that the integral J may be defined in such a way that the route determined by this procedure is the actual route pursued by a particle which moves under the influence of a gravitational field, and which is subjected to the conditions of passing through the points A_1 and A_2 at times t_1 and t_2. Here we assume thot the element of impetus dJ associated with the element of route which is traversed by a particle of " proper " mass μ moving through an element of distance ds in time dt may be written in the form

$$dJ=\mu\,.\,dI=\mu(\omega^2\,.\,dt^2-\varphi^2\,.\,ds^2)^{\frac{1}{2}}, \qquad \ldots \quad (2{\cdot}1)$$

where dI may be called the " potential impetus," to distinguish it from the " realised impetus " dJ, and where ω and φ denote two real functions of the position of the particle at the instant considered, and express the properties of the gravitational field.

¶3. *Lagrangian Equations of Motion.*

In Cartesian co-ordinates x, y, z, the square of the element of distance may be written as

$$ds^2 = dx^2 + dy^2 + dz^2$$
$$= (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \,.\, dt^2,$$

where $\dot{x}$, $\dot{y}$, $\dot{z}$ denote the components of the velocity of the particle traversing the element of distance ds in time dt. The Lagrangian function for the particle may now be defined by the equation

$$L = \mu\{\omega^2 - \varphi^2(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)\}^{\frac{1}{2}} \quad , \quad \ldots \ldots \quad (3\cdot1)$$

and the realised impetus along the route with termini at points A_1 and A_2 at times t_1 and t_2 may be written as

$$J = \int_{t_1}^{t_2} L \,.\, dt, \quad \ldots \ldots \quad (3\cdot2)$$

in virtue of equation (2·1). In this integral it is convenient to suppose that the various possible routes which possess the termini fixed above are prescribed by taking x, y, z to be arbitrary functions of t, which reduce, when $t = t_1$ or t_2 to the co-ordinates of the points A_1 or A_2. The conditions that the integral should be stationary are expressed by the three Lagrangian equations

$$\frac{d}{dt} \cdot \left(\frac{\partial L}{\partial \dot{\theta}}\right) = \frac{\partial L}{\partial \theta} \quad \ldots \ldots \quad (3\cdot3)$$

where θ stands for any one of the co-ordinates x, y, z.

¶4. *Permanent Gravitational Fields.*

The functions ω and φ will be explicitly independent of the time t if the gravitational field is permanent, and we may then deduce two important corollaries to the equations (3·3) of the preceding paragraph.

In the first place, we may infer at once that the initial acceleration **a** of a particle starting from rest is given by the vector equation

$$\mathbf{a} = -\tfrac{1}{2}\varphi^{-2} \,.\, \mathrm{grad.}(\omega^2) \quad \ldots \ldots \quad (4\cdot1)$$

In the second place, the path described by the particle may be found by introducing an auxiliary variable τ defined by the equation

$$c \,.\, \tau = \int \varphi^{-2} \,.\, dI \quad , \quad \ldots \ldots \quad (4\cdot2)$$

in which the integral is taken along the route described by the particle from some convenient terminus, and in which the constant c is inserted to ensure that the variables τ and t have the same dimensions and approximately the same magnitude (*see* ¶6). On using dashes to denote differentiation with respect to τ, we may replace

the Lagrangian function L of the last paragraph (3·1) by the modified Lagrangian function Λ defined by the equation

$$\Lambda=\mu\{\omega^2 \,.\, t'^2-\varphi^2(x'^2+y'^2+z'^2)\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}3)$$

on the understanding that x, y, z, t, are now prescribed as functions of τ. The integral of impetus may be written in the form

$$J=\int_{\tau_1}^{\tau_2} \Lambda . d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}4)$$

where τ_1 and τ_2 are the values of τ at the termini of the route. The four modified Lagrangian equations will be

$$\frac{d}{d\tau}\left(\frac{\partial\Lambda}{\partial\theta'}\right)=\frac{\partial\Lambda}{\partial\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}5)$$

where θ stands for any one of the co-ordinates x, y, z, t.

From equations (2·1), (4·4) and (4·2) we deduce that

$$\mu \,.\, dI\equiv dJ\equiv\Lambda \,.\, d\tau\equiv\Lambda c^{-1}\varphi^{-2} \,.\, dI,$$

whence

$$\Lambda=\mu c\varphi^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}6)$$

But ω and φ are explicitly independent of t and τ, so that the fourth modified Lagrangian equation obtained by writing $\theta=t$ in (4·5) yields the results

$$\frac{\partial\Lambda}{\partial t}=0 \text{ and } \frac{\mu^2\omega^2 t'}{\Lambda}=\frac{\partial\Lambda}{\partial t'}=\text{a constant},$$

whence $\omega^2 t'=c^2p\varphi^2$ from equation (4·6), where p is a constant related to the velocity of projection, u_1, in the manner indicated by the equation (derived from (4·3) and (4·6))

$$p=\frac{\omega_1}{c}\left\{1-\frac{\varphi_1^{\,2}}{\omega_1^{\,2}}u_1^{\,2}\right\}^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}7)$$

in which the suffixes show that the arguments of the functions φ and ω are the co-ordinates of the point of projection.

The three modified Lagrangian equations obtained by setting $\theta=x, y, x$ in (4·5) now yield the results

$$x'', y'', z''=-\frac{\partial U}{\partial x,\ y,\ z,} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}8)$$

where

$$U=\tfrac{1}{2}\varphi^2c^2\left\{\frac{1-c^2p^2}{\omega^2}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4{\cdot}9)$$

Hence, when we know the circumstances of the projection of a particle, we may evaluate the constant p by means of the equation (4·7), and then construct the corresponding function U by means of equation (4·9). The three equations (4·8) then show that the actual path which is described by the particle is identical with that which would be traversed if the particle were moving in a Newtonian field of force of potential U.

II. The Field Equations.

¶5. *Invariant Equations for Permanent Gravitational Fields.*

The second assumption which we make refers to the form in which we shall enunciate the equations of the gravitational field which determine the functions ω and φ. We shall assume that these equations contain no derivatives of ω or φ of orders higher than the second, and that the equations are linear in the second derivatives. The determination of the equations is then completed by the further hypothesis that they shall retain the same form in any set of co-ordinates which preserves the form of dI^2 given in equation (2·1), viz. :—

$$\omega^2 \,.\, dt^2 - \varphi^2(dx^2+dy^2+dz^2)$$

As we are considering statical fields only, we need study the effect of changes in the spatial co-ordinates alone. It will be recognised at once that such transformations in x, y, z as translations and rotations preserve the form of dI^2, and leave invariant the functions ω and φ together with the expressions $\delta\omega$ and $\delta\varphi$, in which δ denotes the Laplacian operator

$$\delta \equiv \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Other quantities which are unaffected in form or magnitude by these transformations are the three scalar products (grad. ω, grad. ω), (grad. ω, grad. φ), (grad. φ, grad. φ); and a great variety of invariant equations satisfying the criteria laid down above may be constructed out of these invariants, the functions ω and φ, and the quantities $\delta\omega$ and $\delta\varphi$.

The quadratic expression $\varphi^2(dx^2+dy^2+dz^2)$ (which is now written more conveniently as $\psi^4(dx^2+dy^2+dz^2)$, so that $\varphi=\psi^2$) also remains unaltered in form when the variables x, y, z are subjected to magnifications or inversions, and, although all the invariants of the last paragraph, except ω, now lose that character, we may construct combinations of them which still retain invariant form and magnitude for these fresh types of transformations. Considering only inversions whose pole is at the origin of the co-ordinate system, we denote the new variables by X, Y, Z, and the radius of inversion by a, so that

$$X : x = Y : y = Z : z = a^2 : r^2 = R^2 : a^2, \quad \ldots \ldots \quad (5·1)$$

where $$r^2=x^2+y^2+z^2,$$

and $$R^2=X^2+Y^2+Z^2.$$

If $\triangle$ denotes the Laplacian operator in the new co-ordinates, so that

$$\triangle \equiv \frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}$$

it is easily established by direct transformation that if

$$f(x, y, z)=F(X, Y, Z),$$

then $$\triangle F=\frac{r^5}{a^5}\delta\left(\frac{af}{r}\right).$$

An immediate corollary to this theorem of Lord Kelvin s is obtained by noting that if

$$\psi^4(dx^2+dy^2+dz^2)=\Psi^4(dX^2+dY^2+dZ^2),$$

then

$$\psi=\frac{a}{r}.\Psi,$$

whence

$$\frac{\delta\psi}{\psi^5}=\frac{\triangle\Psi}{\Psi^5}. \qquad (5{\cdot}2)$$

We have thus obtained one quantity $(\psi^{-5}.\delta\psi)$ which remains invariant for inversions. A second may be constructed on remarking that the relations (5·1) imply also that

$$r.R=a^2$$

$$r.\psi^2=R.\Psi^2$$

while

$$\frac{1}{r^2\psi^6}\cdot\frac{\partial}{\partial^2}=\frac{-1}{R^2\Psi^6}\cdot\frac{\partial}{\partial R}.$$

By transformations in spherical polars it may now be shown that

$$\psi^{-6}\,\mathrm{div.}\,(\psi^2\,\mathrm{grad.}\,\omega)=\Psi^{-6}.\,\mathrm{DIV.}\,(\Psi^2.\,\mathrm{GRAD.}\,\omega), \qquad (5{\cdot}3)$$

where the capitals DIV. and GRAD. denote the vector operators in the co-ordinates X, Y, Z, analogous to the vector operators div. and grad. in the co-ordinates x, y, z.

It is now easily seen that the functions $\psi^5.\delta\psi$ and $(\omega\psi^6)^{-1}.\,\mathrm{div.}\,(\psi^2\,\mathrm{grad.}\,\omega)$, are also invariant for magnifications, as well as for all the other types of transformation studied above. From the well-known researches of Lord Kelvin and M. J. Liouville,* it is known that those transformations exhaust the possible types which leave invariant the equation

$$dx^2+dy^2+dz^2=0,$$

and the form of the expression

$$\psi^4(dx^2+dy^2+dz^2).$$

And it may also be shown that every invariant, which satisfies the criteria laid down above, must be a linear function of the two invariants which we have found. Hence the most general invariant equations for permanent isotropic gravitational fields are

$$\left.\begin{aligned}\delta\psi&=\lambda_1.\psi^5,\\ \text{and}\quad \mathrm{div.}\,(\psi^2\,\mathrm{grad.}\,\omega)&=\lambda_2\omega\psi^6\end{aligned}\right\} \qquad (5{\cdot}4)$$

where λ_1 and λ_2 are constants.

A reference to a classical memoir of Levi-Cività† will show that in his notation we may write

$$M=-4\psi^{5}.\delta\psi$$

and

$$\triangle_2\omega=\psi^{-6}.\,\mathrm{div.}\,(\psi^2\,\mathrm{grad.}\,\omega),$$

so that our equations are

$$\left.\begin{aligned}M&=-4\lambda_1\\ \text{and}\quad \triangle_2\omega&=\lambda_2\omega\end{aligned}\right\} \qquad (5{\cdot}5)$$

* " Extraits de deux Lettres adressées à M. Liouville par M. William Thomson." "Note au sujet de l'article précédent, par J. Liouville," pp. 256-264 and 265-290, Journal de Mathématiques pures et appliquées, Tome XII. (1847).

† T. Levi-Cività, " Statica Einsteiniana," Atti d. Reale Accad. d. Lincei, Roma, Serie (5), 1917. Tom. 26 (1), pp. 458-470.

¶6. *Supplementary Conditions.*

The two equations (5·4) or (5·5) of the last paragraph will take the place in this Paper of the seven equations given by Levi-Cività (provided we take λ_1 and λ_2 to be zero, as in Einstein's earlier theory). The determinations of the functions ω and φ will be completed by assigning suitable boundary conditions and two additional assumptions.

The first of these assumptions (and the third employed in this Paper) is an extension of the hypothesis of ¶2. There we assumed that the routes traversed by material particles were the geodesics of the quadratic differential form

$$dJ^2=\mu\{\omega^2dt-\varphi^2(dx^2+dy^2+dz^2)\}.$$

Among these geodesics we may single out for special mention those which also satisfy the condition

$$dJ=0.$$

These "null-routes," along which the impetus is zero, we assume to be the tracks of rays of light.

Since along these routes dI and $d\tau$ (by (4·2)) are zero, we must write their equations in the forms of ¶3 rather than in the modified forms of ¶4. Thus, we deduce at once from equations (3·1) and (3·2) that along a "null-route"

$$L=0,$$

while the velocity of propagation of the ray of light is

$$(\dot{x}^2+\dot{y}^2+\dot{z}^2)=\frac{\omega}{\varphi} \quad \ldots \ldots \ldots \ldots \quad (6\cdot1)$$

Since this velocity is independent of the direction of propagation the field is said to be "isotropic."

The last assumption that we make is that as we recede from regions of space occupied by matter, the effects of gravitational influence diminish, in such a way that at considerable distances the gravitational field is sensibly Newtonian in character, while the velocity of light is sensibly equal to 3×10^{10} cms./sec., a constant denoted by c.

It is evident that the multiplication of ω and φ by the same number will have no influence on the form of the routes of mass-particles or rays of light. As a convention, therefore, we shall make $\varphi\rightarrow1$ as $x, y, z\rightarrow\infty$. Then, from equation (6·1) and our last assumption we see that under these conditions $\omega\rightarrow c$ and $dI\rightarrow c.dt$. We thus justify the inclusion of the constant c in equation (4·2).

Even now the determination of the functions ω and ψ is not unique; for it will be seen that if V is any Newtonian potential satisfying the equation

$$\delta\,.\,V=0,$$

then, since $r.V$ and r^2 grad. V both tend to constant values as we recede from the regions occupied by matter, approximate solutions of the gravitational equations (5·4) when λ_1 and λ_2 are zero, are

$$\text{and}\qquad \left.\begin{aligned}\psi&=1+\kappa_1V\\ \omega&=c(1+\kappa_2V)\end{aligned}\right\} \quad \ldots \ldots \ldots \ldots \quad (6\cdot2)$$

To identify the constant κ_2 we observe that the initial acceleration of a particle as given by equation (4·1) is

$$\mathbf{a} \sim -c \text{ grad. } \omega = -c^2\kappa_2 \text{ grad. } V,$$

whence κ_2 must be c^{-2} in order that we may satisfy the last assumption of this paragraph. But we still have no means by which we may determine the constant κ_1. To identify this constant we have recourse to the cosmological theory of the succeeding paragraph.

¶7. *Cosmological Theory.*

We have hitherto supposed that the element of distance between two points is given by the Euclidean relation

$$ds^2 = dx^2 + dy^2 + dz^2\,;$$

but if we suppose that a better representation of the phenomena may be obtained with non-Euclidean geometry, we must replace this equation by

$$ds^2 = \frac{dx^2 + dy^2 + dz^2}{(1 + r^2/4R^2)^2}, \qquad (7{\cdot}1)$$

where R is the "space-constant" (determining the "size" of the universe) and $r^2 = x^2 + y^2 + z^2$.

Now the function $\psi = (1 + r^2/4R^2)^{-\frac{1}{2}}$ is a solution of the equation

$$M = 3\,.\,R^{-2},$$

and we shall accordingly adopt this relation as one of the field equations in non-Euclidean space.

To obtain the appropriate value of the constant λ_2 in the second equation (5·5) we note that if θ and ϕ are the usual angular co-ordinates in the spherical polar system, while

$$r = 2R\,.\,\tan\tfrac{1}{2}\chi,$$

then

$$ds^2 = R^2 d\chi^2 + R^2 \sin^2\chi(d\theta^2 + \sin^2\theta\,.\,d\phi^2). \qquad (7{\cdot}3)$$

Hitherto, our expression for dI^2, the square of the linear element of the dynamic manifold, has had the limiting form (see ¶6), as $x, y, z \to \infty$.

$$dI^2 = c^2 dt^2 - (dx^2 + dy^2 + dz^2),$$

but now, following de Sitter,* we shall take as the limiting form

$$\begin{aligned} dI^2 &= \cos^2\chi\,.\,c^2 d\tau^2 - R^2 d\chi^2 - R^2\sin^2\chi(d\theta^2 + \sin^2\theta\,.\,d\phi^2) \\ &= \omega^2\,.\,d\tau^2 - \psi^4(dx^2 + dy^2 + dz^2), \end{aligned}$$

where

$$\left.\begin{aligned} \psi &= (1 + r^2/4R^2)^{-\frac{1}{2}}, \\ \text{and} \quad \omega &= c\cos\chi = c\,\frac{1 - \dfrac{r^2}{4R^2}}{1 + \dfrac{r^2}{4R^2}} \end{aligned}\right\} \qquad (7{\cdot}4)$$

* A. S. Eddington, "The Mathematical Theory of Relativity," 1923. § 67, "Cylindrical and Spherical Space-time."

This function satisfies the equation

$$\frac{\triangle_2 \omega}{\omega} = -3R^{-2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7 \cdot 5)$$

which we shall therefore take to be the second field equation in non-Euclidean space.

From the values of ψ and ω, given in equation (7·4), and by the use of equation (4·1), we find that the initial acceleration of a particle is

$$\frac{c}{R^2} r\omega$$

indicating the tendency to scatter shown by the high recessive velocities of spiral nebulæ.

To complete the determination of the constants λ_1 and λ_2 of the preceding paragraph, we construct the complete integrals of equations (7·2) and (7·5), on the assumption that ψ and ω are functions of r only. The solutions thus obtained apply to the regions of space remote from matter. The first equation (7·2) may be written as

$$\frac{1}{\psi^5}\left(\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr}\right) + \frac{3}{4R^2} = 0$$

and possesses an integrating factor

$$4r^2\psi^5\left(\psi + 2r\frac{d\psi}{dr}\right)$$

by means of which we obtain the first integral

$$4r^3\left(\frac{d\psi}{dr}\right)^2 + 4r^2\psi\frac{d\psi}{dr} + \frac{\psi^6 r^3}{R^2} = -2m,$$

where m is a constant integration. This equation may also be written in the form

$$\frac{d}{dr}(r\psi^2) = \psi^2 . \left(1 - \frac{2m}{\psi^2 r} - \frac{\psi^4 r^2}{R^2}\right)^{\frac{1}{2}}$$

To complete the solution, we introduce a new variable ρ, defined by the relation

$$\rho = r\psi^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7 \cdot 61)$$

and the function

$$\gamma = 1 - \frac{2m}{\rho} - \frac{\rho^2}{R^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7 \cdot 62)$$

whence

$$\frac{d\rho}{dr} = \frac{\rho}{r}\sqrt{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7 \cdot 63)$$

and $$\psi^4(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta \, . \, d^2\phi) = \frac{d\rho^2}{\gamma} + \rho^2 d\theta^2 + \rho^2 \sin^2\theta d\phi^2 \quad . \quad . \quad . \quad (7 \cdot 64)$$

If an explicit expression for ρ is required, we deduce from equation (7·63) that

$$\log\frac{r}{r_0} = \int^{\rho_0} \frac{d\rho}{\rho\sqrt{\gamma}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7 \cdot 65)$$

(where ρ_0 is the larger positive root of the equation $\gamma=0$). So that ρ may be expressed in terms of r by means elliptic functions.

The second equation (7·5) may be written as

$$\frac{d}{dr}\left(r^2\psi^2\frac{d\omega}{dr}\right)=-\frac{3r^2\psi^6\omega}{R^2};$$

or, on changing the independent variable from r to ρ, as

$$\frac{d}{d\rho}\left(\gamma^{3/2}\frac{d}{d\rho}(\gamma^{-\frac{1}{2}}\,.\,\omega)\right)=0$$

whence the complete integral is seen to be

$$\omega=A\,.\,\sqrt{\gamma}+B\sqrt{\gamma}\int_0 \gamma^{-3/2}.\,d\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\cdot7)$$

We have now four arbitrary constants of integration to identify—the A and B of (7·7), the m which occurs in γ (7·62) (and hence in ρ, ψ and ω), and the r_0 of (7·65). Now in the absence of a gravitational field, as we see from the particular solutions of (7·4), $m=0$, while

$$\rho=r\,.\,(1+r^2/4R^2)^{-1}$$

and

$$\gamma=1-\rho^2/R^2$$

Even when a gravitational field is present, the effects of such a field in regions remote from the attracting matter, say where $\rho\sim R$ or $r\sim 2R$, must be negligible compared with the effects of space curvature. Hence to determine r_0 in (7·65) we assume that ψ is approximately equal to $(1+r^2/4R^2)^{-\frac{1}{2}}$, when r is approximately $2R$. Then r_0 must be 2R. To determine A and B in (7·7) we assume that ω is approximately equal to $c\,\frac{1-r^2/4R^2}{1+r^2/4R^2}$ when $r\sim 2R$. Then B must be zero (for the integral is divergent), while $A=c$. Hence the admissible integrals are

$$\psi=\sqrt{\rho/r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\cdot81)$$

where ρ is defined by the integral

$$\log\frac{r}{2R}=\int^{\rho_0}\frac{d\rho}{\rho\sqrt{\gamma}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\cdot82)$$

and

$$\omega=c\sqrt{\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\cdot83)$$

In regions where gravitational effects are of the first order of infinitesimals, while curvature effects are of the second order of infinitesimals—i.e., $\frac{2m}{\rho}$ is small compared with unity, while $\frac{\rho^2}{R^2}$ is small compared with $\frac{2m}{\rho}$, we have the approximations

$$\left.\begin{aligned} r&\sim\rho-m\\ \psi&\sim 1+\frac{m}{2r}\\ \text{and}\qquad \omega&\sim c\left(1-\frac{m}{r}\right)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\cdot9)$$

If the total mass of attracting matter is M, the Newtonian potential will be approximately

$$V \infty -\frac{\gamma M}{\varepsilon} \text{ (where } \gamma \text{ is now the constant of gravitation)}$$

Hence by comparing equations (7·9) and (6·2) we see that.

$$m = -\gamma \frac{M}{c^2}$$

$$\kappa_1 = -\frac{1}{2c^2} \text{ and } \kappa_2 = \frac{1}{c^2}$$

III. The Solar Field.

¶8. *Solution of the Field Equations.*

In applying the general methods of the preceding paragraphs to the particular problems of the solar gravitational field, we take the centre of the sun as the origin of a system of polar co-ordinates of radius vector r; and we assume that the gravitational field of the sun has spherical symmetry, so that the functions ω and φ depend only upon r. The general equations of the field (5·4) now simplify to

$$\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = 0$$

and

$$\frac{d}{dr}\left(r^2 \psi^2 \frac{d\omega}{dr}\right) = 0$$

The general solutions of these equations, subject to the boundary conditions

$$\psi \rightarrow 1 \text{ and } \omega \rightarrow c \text{ as } r \rightarrow \infty$$

are

$$\psi = \left(1 + \frac{m_1}{2r}\right)$$

and

$$\omega = c\frac{1 - \frac{m_2}{2r}}{1 + \frac{m_1}{2r}} \sim c\left(1 - \frac{m_1 + m_2}{2r}\right),$$

where m_1 and m_2 are constants of integration.

The application of the general results of the last paragraph (equation (7·9)) now shows that if M is the mass of the sun and γ is the constant of gravitation,

$$m_1 = m_2 = m = \frac{\gamma M}{c^2}$$

We have thus obtained Hill and Jeffery's solution of Einstein's equations*

$$\left.\begin{aligned} \psi &= \left(1 + \frac{m}{2r}\right) \\ \text{and} \qquad \omega &= c\frac{1 - \frac{m}{2r}}{1 + \frac{m}{2r}} \end{aligned}\right\} \quad \ldots \ldots \ldots \ldots \quad (8{\cdot}1)$$

* F. W. Hill and G. B. Jeffery, "The Gravitational Field of a Particle on Einstein's Theory," Phil. Mag. (6), Vol. 41, pp. 823-826 (1921).

whence

$$dI^2=\left(\frac{1-\frac{m}{2r}}{1+\frac{m}{2r}}\right)^2 c^2dt^2-\left(1+\frac{m}{2r}\right)^4 (dr^2+r^2d\theta^2+r^2d\phi^2)$$

(in spherical polar co-ordinates r, θ, ϕ).

We may also deduce these results from the general " cosmological " solutions of (7·81, 7·82 and 7·83) by making $R\to\infty$.

¶9. *Planetary Orbits.*

To determine the forms of the orbits described by planets in the solar field, we assume that to a first approximation we may neglect their mutual perturbations, and that we may regard them as particles. We then apply the general results established in ¶4. Since planetary velocities are small compared with the velocity of light, the constant p of equation (4·7) may be taken to be unity, and the " apparent Newtonian potential " U of equation (4·9) may then be written in terms of $u=1/r$, as

$$U\sim\frac{c^2}{2}\left(1+\frac{1}{2}mu\right)^4-\frac{c^2}{2}\left(1+\frac{1}{2}mu\right)^6.\left(1-\frac{1}{2}mu\right)^{-2}$$

(in virtue of equations (8·1))

$$=-c^2(mu+3m^2u^2) \qquad \dots\dots\dots \quad (9·1)$$

neglecting powers of $(m\,.\,u)$ above the second, an approximation justified, since for the sun $m=1·47$ km., and for mercury $u^{-1}=5·77\times10^7$ km.

The path described by a planet is found now just as in classical dynamics, provided that the variable τ of equation (4·2) is treated as the " time " and that U is treated as the " potential." Since U is a function of r only, the path will be plane and will be traversed with uniform areal " velocity "

$$\frac{1}{2}r^2\frac{d\theta}{d\tau}=\frac{1}{2}h$$

(using θ to denote the angle which the radius vector of the planet makes with any fixed line in the plane of the orbit). The apparent central acceleration will be

$$P=\frac{dU}{dr}=-u^2\frac{dU}{du}$$

and the equation to the orbit is therefore

$$\frac{d^2u}{d\theta^2}+u=\frac{-P}{h^2u^2}$$

$$=\frac{mc^2}{h^2}(1+6mu) \text{ from equation (9·1)} \qquad \dots\dots \quad (9·2)$$

The solution of this equation (an especial case of " Newton's revolving orbits " is)

$$l\,.\,u=1+\varepsilon\cos\kappa\theta$$

where

$$\frac{lmc^2}{h^2}=\kappa^2=1-\frac{6m^2c^2}{h^2},$$

and represents an ellipse, focus at the sun, semi-latus-rectum l and eccentricity ε, revolving in its own plane, so that the perihelion advances

$$\frac{2\pi}{\kappa}-2\pi\sim\frac{6\pi\gamma M}{c^2 l}\text{ radians per complete revolution of the planet.}$$

¶10. *Light Rays.*

Apart from a constant factor, the Lagrangian function of (3·1) may be written in polar co-ordinates as

$$L=\{\psi^2-\varphi^2(\dot{r}^2+r^2\dot{\theta}^2)\}^{1/2}$$

It has been explained in ¶ 6 that the paths of rays of light are determined from those special solutions of the Lagrangian equations

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}}\right)=\frac{\partial L}{\partial r}\text{ and }\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right)=\frac{\partial L}{\partial \theta}\quad\ldots\ldots\ldots\quad\text{(cf. eq. 3·3)}$$

which also satisfy the relation (6·1)

$$v^2=\dot{r}^2+r^2\dot{\theta}^2=\omega^2\varphi^{-2}\quad\ldots\ldots\ldots\ldots\quad(10\cdot1)$$

In the solar gravitational field, it is evident that we may limit ourselves to the consideration of paths which lie in a plane passing through the centre of the sun, and such that ω and φ will depend only upon the radius vector r. Hence the second of the Lagrangian equations given above yields the integral

$$\varphi^2\,.\,r^2\dot{\theta}\,.\,L^{-1}=\text{const.}\quad\ldots\ldots\ldots\ldots\quad(10\cdot2)$$

Also from equation (4·7) we obtain the relation

$$\omega^2\,.\,L^{-1}=\text{const.}\quad\ldots\ldots\ldots\ldots\ldots\quad(10\cdot3)$$

Although both of these equations become illusory when $L=0$, we may still obtain an effective relation by equating the ratios of corresponding sides, when we obtain

$$\varphi^2\,.\,\omega^{-2}\,.\,\dot{\theta}r^2=\text{const.}\quad\ldots\ldots\ldots\quad(10\cdot4)$$

That this constant is finite may be deduced from equation (10·1) by noticing that when $\dot{r}=0$—i.e., at an apse (say, when $r=r_0$), then

$$r\dot{\theta}=\omega_0\,.\,\varphi_0^{-1}$$

whence the constant of (10·4) is seen to be $r_0\varphi_0\omega_0^{-1}$ (the suffixes showing that the arguments of the functions ω and φ are both r_0).

The equation to the path of a ray of light is now obtained by substituting in (10·1)

$$r=1/u,\ \dot{r}=-r^2\dot{\theta}\,.\,du/d\theta$$

and the value of $\dot{\theta}$ given by equation (10·4). We thus obtain

$$\left(\frac{du}{d\theta}\right)^2+u^2=\frac{\varphi^2}{\varphi_0^2}\,.\,\frac{\omega_0^2}{\omega^2}\,.\,u_0^2$$

$$=u_0^2\,.\,(1+4mu-4mu_0)\quad\ldots\ldots\ldots\quad(10\cdot5)$$

to our degree of approximation. The solution of this equation is

$$u=2mu_0^2(1+\varepsilon\cos\theta)$$

where

$$\varepsilon\sim1/2mu_0^2$$

showing that the path is an hyperbola of eccentricity ε. Hence the angle between the asymptotes of the hyperbola, which gives the angular deviation of the light from a distant star, is $4mu_0$ radians.

¶11. *Conclusion.*

In this brief sketch of one of the theories of relativity, the three equations of motion of a particle given by Newton's theory are replaced by the three equations of (4·8); while the Laplacian equation satisfied by the Newtonian potential is replaced by the two equations (5·5), satisfied by the two functions ω and φ; so that as close an analogy as possible has been maintained with the principles and methods of classical dynamics. Unfortunately, in order to obtain suitable qualitative boundary conditions, it has been necessary to introduce de Sitter's cosmological theory and "spherical space time." With this single exception, the argument follows the lines of Einstein's General Theory and issues in the same conclusions.

DISCUSSION.

Prof. W. Wilson said that he cordially welcomed the reading of Papers of the present kind to the Physical Society, but he questioned whether the author's method was as simple in principle as that of Schwarzschild, in spite of its saving of laborious computation. The practice of regarding an event-path as a geodesic had been referred to by the author as an "assumption," but he would like to ask what significance could be attached to a path which was not a geodesic.

Dr. C. Chree referred to some outstanding analytical problems which were insoluble, or soluble only with difficulty, by the classical mechanics, and inquired whether the forms of calculus brought into prominence by the theory of relativity had provided simpler methods of dealing with any of these.

Author's reply (communicated).—In reply to Dr. Wilson: Schwarzschild's problem was the *solution* of the gravitational equations $G_{\mu\nu}=0$ in a static field possessing spherical symmetry; the object of this Paper is the *construction* of the gravitational equations in a static and isotropic field; hence the problems are of different characters. Deviations from geodesic paths may be attributed (if the moving particle is charged) to the influence of electromagnetic fields.

In reply to Dr. Chree, I quote from MM. Ricci and Levi-Cività (Math. Ann., Band 54, 1900, S.159): "Ces méthodes (de calcul différentiel absolu) n'ont pas la prétention d'éliminer les difficultés essentielles aux questions auxquelles elles sont appliquées. Au contraire, elles ne conduisent qu'à des transformations d'équations laissant nécessairement subsister toutes ces difficultés."

XXXIV.—ON THE DIFFRACTION OF LIGHT BY SPHERICAL OBSTACLES.

By Prof. C. V. Raman, *F.R.S.*, and Mr. K. S. Krishnan.

Abstract.

The diffraction of light inside the shadow, thrown by a small source of light, of a sphere and a circular disc of the same diameter, was studied, with special reference to the relative intensities of the central bright spots. With the source at about 2 metres from the obstacles, with a quarter-inch polished steel ball, the bright spot could be detected visually up to 3 cm. behind the obstacle, while with a steel disc of the same diameter, with the edges perfectly sharp, smooth and circular, the spot could be traced up to 2 cm.

The relative intensities of the two spots were studied at different distances behind the obstacles, qualitatively by photography and quantitatively by visual photometry. At small distances behind the obstacles, the spot inside the shadow of the sphere is much feebler than the disc-spot, however approximating to the latter as we reach farther back from the obstacles, but even at 100 cm. remaining appreciably feebler.

A general explanation is suggested.

I. Introduction.

It has long been known* that at the centre of the shadow of a spherical obstacle thrown by a small source of light there is a bright spot similar to that found in the shadow of a circular disc ; and, in fact, a spherical obstacle is often used instead of a disc to demonstrate the formation of the bright spot at the centre of the shadow of a circular boundary. It is usually assumed by experimenters† that at a point on the axis of the shadow a circular disc and a sphere of equal radius would give practically identical results. This, however, is not actually the case, and it is the purpose of this Paper to draw attention to the notable differences that exist between the effects observed in the two cases.

II. The Intensity of the Bright Spot.

To compare the effects obtained in the shadow of a spherical obstacle and a circular disc of equal size, it is convenient to mount them side by side on a glass plate, so that the bright spots at the centres of their shadow may be seen at the same time. In most of our observations we used a quarter-inch (diameter) steel ball and an accurately made steel disc of the same size, cut on the lathe so as to have a sharp circular edge of razor-like smoothness and sharpness. They were attached by specks of wax, with sufficient space between them, to a glass plate, and held at a distance of about two metres from the source.

The diffraction patterns within the shadow of disc and sphere were seen simultaneously through a lens of sufficiently wide field of view. When a bright source of light is used, it is convenient to use a plate with two holes cut in it, to correspond with the shadow of the sphere and the disc, and place it in the field of view so as to cut off all extraneous light except that diffracted into the region of shadow. The removal of the glare outside the region of shadow is very helpful, and with this

* Rayleigh, Sc. Papers, Vol. V, p. 112. *See* also A. O. Rankine, Proc. Phys. Soc., Vol. 37, p. 267 (1925).

† Hufford, Phys. Rev., Vol. 7, p. 545 (1916).

FIG. 1.

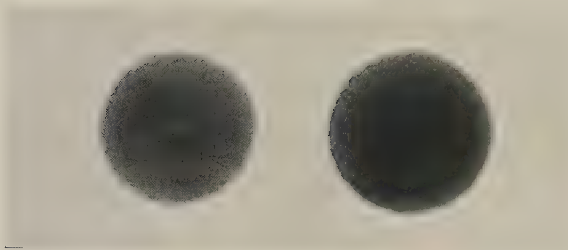

FIG. 2.

FIG. 3.

FIG. 4.

[To face page 351

arrangement it is possible to trace the bright spots in the centre of the shadow up to within 3 cm. of the object in the case of the sphere, and to less than 2 cm. in the case of the disc, thus testifying to the accuracy of the edges. A series of photographs were taken of the diffraction patterns with the source of light 179 cm. in front of the obstacles, and with the object plane of the camera at different distances behind them. Some of these are reproduced here (Figs. 1, 2, 3, 4). In the photographs the diffraction pattern on the right corresponds to the sphere and that on the left to the disc. We can easily see that the central white spots in the case of the sphere are much less bright than in the case of the disc. Thus, in Fig. 1, which corres-

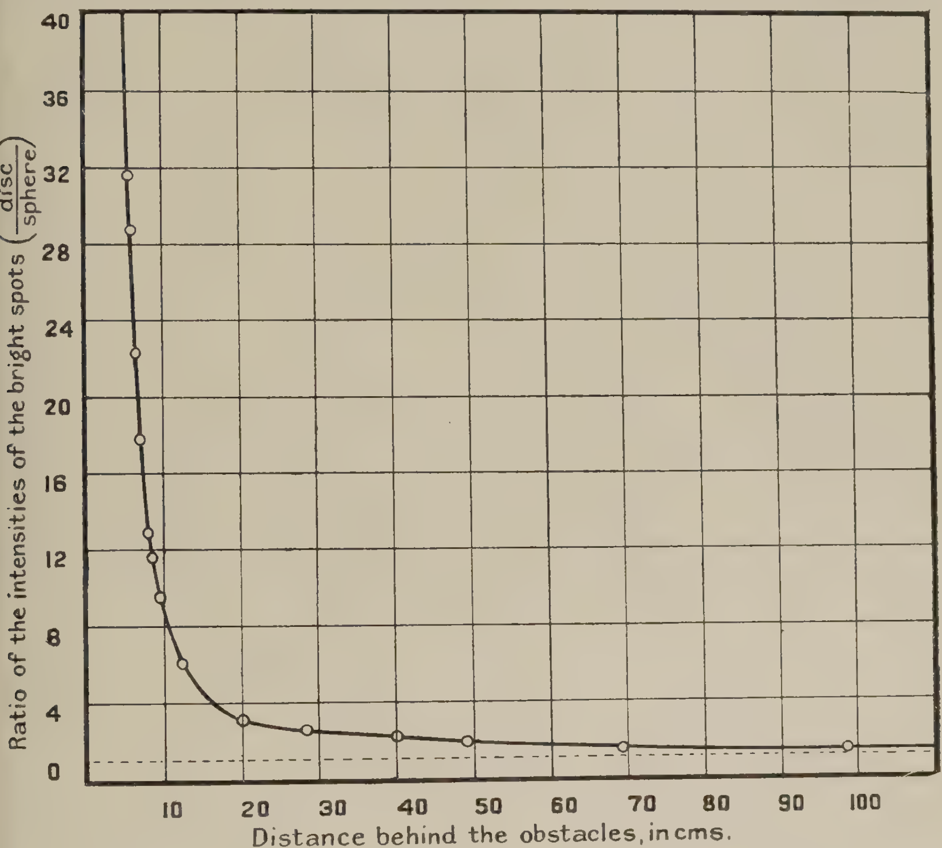

FIG. 5.

ponds to a distance of about 11 cm. behind the obstacles, the spot in the case of the sphere is invisible in the photograph. At 13 cm., as shown in Fig. 2, it is just visible. At 25 cm. (Fig. 3) it is still much feebler than for the disc, and at 40 cm. (Fig. 4) the difference in intensity of the two bright spots is still conspicuous. Further, we see in the photographs that the general illumination within the geometrical shadow is much greater for the disc than for the sphere. The spots in the shadow of the sphere were distinctly reddish in comparison with those for the disc, and the photographic intensity thus differed more than the visual intensity.

A quantitative study of the relative intensities of the central white spots of the two diffraction patterns was made with the help of an Abney rotating sector photometer placed just in front of the obstacles, and looking for the diffraction patterns through the eye-glass with the two apertures in its focal plane, mentioned already. The source of light was at a distance of 232 cm. in front of the obstacles. The results are shown in the graph on p. 351 (Fig. 5). Owing to the difference in colour, some uncertainty arises in the visual estimates of equality of intensity. Further, for short distances behind the obstacles the comparison was by no means easy, owing to the spots having a very small size, and appearing against a luminous background. Owing to these circumstances, the measurements shown in the graph are only approximate. Nevertheless, they sufficiently indicate the general character of

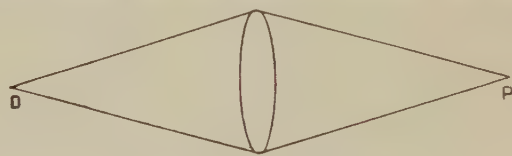

FIG. 6*a*.

the phenomenon. The dotted line in Fig. 5 is the asymptote to the curve, and is slightly above the line of equality of intensities.

III. Discussion of Results.

Without going into the mathematical theory of diffraction by a spherical obstacle, it is not difficult to give a general physical explanation of the above experimental results. In the case of the disc (Fig. 6*a*) the rays diffracted by the illuminated edge reach the point of observation directly. In the case of the sphere, however, the position is somewhat different. Drawing tangent cones enveloping the spherical obstacle, with the source and the point of observation as apexes (Fig. 6*b*), we see

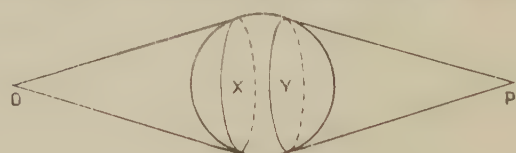

FIG. 6*b*.

that they now touch the sphere at different circles of contact, X and Y respectively. Thus, the circle of contact Y, from which diffracted rays originating at the surface can reach the point of observation, lies within the region of geometrical shadow, and not at its edge, as in the case of the disc. The disturbance incident on the surface of the sphere has to creep round it, as it were, over the arc XY before the rays diffracted out by the sphere can reach the point of observation, and must suffer a very considerable diminution in the process. Thus, we can see that the intensity of the central white spot in the diffraction pattern of a sphere will be less than in the case of the disc at the same distance behind by a quantity depending on the length of the arc XY between the circles of contact of the tangentially incident and diffracted rays. Now the length of this arc will be the greater the nearer the point of observation

ıpproaches the sphere, so that the intensity of the sphere-spot, as compared with the disc-spot, ought to decrease as we approach the obstacles. Proceeding in he opposite direction, the intensity at large distances will approach that of the dfsc, ɔut still will be smaller than the latter by an amount which will depend on the listance of the source from the obstacle.

That the foregoing way of viewing the matter is not fanciful, but is really a statement of the physical processes occurring in the case, is evident from the following observations. A microscope is focussed tangentially on the circle of contact X ılready mentioned, which appears as a luminous edge in the field of view. If now he microscope is shifted laterally into the region of the geometrical shadow, we ind that it has also to be drawn back longitudinally towards Y in order to keep the liffracting edge of the sphere in focus, whereas in the case of the disc such longitu- linal movement is not found to be required. Further, the luminous edge of the sphere is found to diminish in brightness much more rapidly than in the case of the lisc when the observer's eye is moved laterally into the region of shadow. Similar lifferences are also found when we compare the diffraction into the region of shadow ɔy a sharp straight edge and by the edge of a cylinder.

We recognise that the explanation we have offered is only qualitative. The eality of the effects described is, however, unquestionable, and we have no doubt hat a quantitative explanation will be forthcoming when the diffraction problem s considered on the basis of the electromagnetic theory for the case of the large phere. This problem has been handled by Poincaré, Nicholson, Macdonald, Brom- vich, G. N. Watson and others. The Paper by Macdonald, on "The Diffraction of Electric Waves Round a Perfectly Reflecting Obstacle,"* might in particular be eferred to, as the analysis contained in it approaches most closely to the point of view rom which we have explained our experimental results. The formulæ given by Macdonald are, however, not in a form capable of immediate application to the problem without considerable labour. As the experimental work was completed ast summer, and as we are at present engaged on other work, we have thought it best not to defer publication of the results any longer.

* Phil. Trans. R.S., A.210, 113 (1910). For other references *see* Bateman, "Electrical and ptical Wave Motion."

XXXV.—ON THE ABSORPTION AND SERIES SPECTRA OF NICKEL

By Prof. A. L. NARAYAN, *D.Sc., F.Inst.P.*, and K. R. RAO, *M.A.*

ABSTRACT.

The Paper gives an account of the experiments on the absorption spectrum of nickel by th under-water spark from λ6000-λ2000. In the region λ3800 to λ2100, 180 wavelengths were obtaine in absorption. The majority of these lines were classified by Bechert and Sommer. Intensit values of the absorbed lines showed that the intensity rule and the selection rule for inne quantum numbers were accurately fulfilled. The results confirm in a striking manner th recent classifications of Bechert and Sommer in the arc spectrum of nickel.

ONE of the main approaches to the problem of atomic structure is by mean of observations of absorption spectra of the vapours of the elements in th normal or excited states. According to Bohr's theory, for the vapour of an elemen to absorb lines corresponding to a given series in its spectrum, it is necessary tha in the vapour there should be a fairly large number of atoms with orbit corresponding to the first term of the pulse of radiation to be absorbed. Th position of the absorption spectrum is therefore of fundamental importance fo the knowledge of the series scheme, as absorption lines, so far as they arise in non luminous vapours, correspond to the unexcited natural state of the atom, the initia level of absorption being the "natural orbit" of the atom. The varieties o spectral series, their representation by formulæ and the possibility of other types o regularities in the arc and spark spectra of the different elements are subjects o far-reaching importance whose study, as Fowler put it, "bids fair to become th main avenue of approach to the problem of atomic structure."

In general, experimental arc and spark spectra of any particular elemen contain many lines in common; the enhanced lines are often excited in an ordinar electric arc and with greater prominence in the vacuum arc, while true arc line (lines belonging to the neutral atom) appear in high-potential sources such a condensed sparks. According to Bohr's theory of spectra, arc and spark spectr are quite distinct, arc lines being emitted by the interorbital transitions of th valence electron in the neutral atom, while spark lines result in energy changes i atoms that have lost one or more of its outermost electrons. To provide dat likely to be useful in identifying the series spectra of neutral atoms, the author began two years ago a systematic study of the absorption of light by non-luminou vapours of different elements, by using a long column of vapour under purel thermal excitation, and the results of some of these are published in a number o Papers.(1) In view of the fact that most of the elements of the periodic tabl particularly those of the higher groups, possess high boiling points, so that to obtai sufficient vapour for absorption experiments very high temperatures were necessar absorption spectra of these elements were not studied till recently. But during th past few months, with the development of experimental technique, absorptio spectra of a number of refractory elements were studied by McLennan, Zumstei Angerer and Joos and others, as a result of which several lines have been cla-sifie

In the identification of the regularities in the arc spectra, apart from the u of high-temperature furnace used by these authors, there is yet another mean particularly useful with metals having high boiling points. This method involv

he use of high-frequency oscillatory spark under water between electrodes of he metal, and was in recent times used by Hulbert,[2] L. and E. Bloch,[3] Clark and Cohen[4] and others. In continuation of our experiments on absorption spectra we began recently an attack on the absorption spectra of the elements of the higher groups of the periodic table, particularly Fe, Co, and Ni, using the latter method. When experiments on Fe and Co were complete, Sur's Papers[5] giving an account of similar experiments appeared. Though in all these cases we studied the absorption to $\lambda 2000$, while Sur went up to $\lambda 2400$, our efforts were concentrated on nickel, and it is the purpose of the present Paper to give an account of the results of these experiments.

Angerer and Joos,[6] McLennan and McLay[7] and Buffam and Ireton[8] have also investigated the absorption spectrum of this element. McLennan and McLay with a furnace current of 40-45 amperes obtained 73 wavelengths in absorption, while Buffam and Ireton obtained 50 lines by the under-water spark method. As

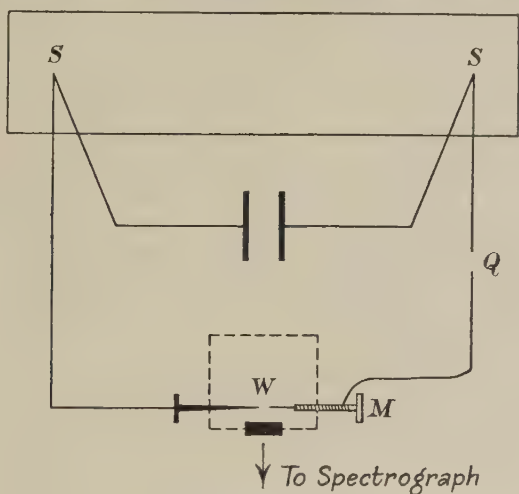

FIG. 1.

the accompanying tables and spectrograms show, about 180 wave-lengths were obtained in these experiments as absorption lines.

In connexion with this method of investigating the absorption and series spectra of an element, it is worth noting that if the spark is properly tuned it can be made to emit a perfectly continuous spectrum, which is of great advantage in absorption experiments. Appearance of absorption lines is favoured by increase of electrode diameter, increase of frequency and diminution of potential. When under these conditions the discharge passes, the discharge nucleus itself gives a continuous spectrum and is surrounded by a vapour mantle which contains mostly vapour particles in a normal state. Another peculiarity of the under-water discharge is that under these conditions it exhibits both emission and absorption lines, absorption lines belonging to the series systems in the arc spectrum, while emission lines mostly belong to the first spark spectrum. As will be seen from the note on the spectrum of Fe at the end, all the lines of the *DP* multiplet of the quartet system[9] of Fe^{+} are exhibited as emission lines in the under-water

spark spectrum of iron. This evidence is a sufficient proof that the under-wat spark discharge is of great use in the study of the spectral structures for neutr and ionized elements.

EXPERIMENTAL.

Fig. 1 is a diagrammatic sketch of the electrical connexions for the spa under water. The secondary terminals *S*, *S* are connected to the under-water spa gap *W*, with an additional gap *Q* in series. The condenser capacity could be vari from 0·005 to 0·02 microfarad. The spark under water took place between pur nickel rods, the distance between them being finely adjusted by a micromet screw *M*.

In taking the photographs, a plane grating spectrograph was used for t region λ6000 to λ3400 and a large Hilger quartz spectrograph for the regi λ3600-λ2000. For the region λ2400-λ2000 Hilger's Schumann plates were use Up to λ2400 the best exposure was two or three minutes, while for the region shorter wavelength the best exposure was found to be 15 to 20 minutes.

Recently Walters and Bechert and Sommer[(10)] have classified a number wavelengths in the arc spectrum of nickel. Bechert and Sommer have found th in this element the spectral terms are of odd multiplicity and found evidence f singlet, triplet and quintet systems and intercombinations. The fundament term is an *f* term of the triplet system.

Owing to the diffuse nature of the lines in the absorption spectrum, attemp were not made to measure the wavelengths, but these were identified after a caref examination with the measures of Siegmund Hamm.[(11)] In the following table a given the wave-lengths (rounded off to the second decimal place), wave numbers a intensities (as obtained in absorption) of the absorption lines, together with t series notation by Bechert and Sommer :—

TABLE OF ABSORBED WAVE-LENGTHS.

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
		3858·28	3	25910·97	$\bar{D}_2{}^1-\bar{f}_3{}^{1a}$
		3807·14	1	26259·06	$\bar{D}_2{}^1-d_3{}^1$
		3783·52	0	422·94	$\bar{D}_2{}^1-\bar{f}_3{}^1$
		75·56	0	478·63	$D_2{}^1-d_2{}^1$
	3619·37	3619·39	7	27621·11	$D_2{}^1-\bar{F}_3{}^1$
		3612·73	2	672·03	$f_2{}^1-d_2{}^1$
	10·46	10·45	2	689·51	$\bar{d}_2{}^1-\bar{p}_2{}^1$
	3602·26	—	—	—	
	3597·71	3597·70	2	787·65	$d_1{}^1-\bar{p}_1{}^1$
		3571·87	3	989·54	$f_3{}^1-\bar{f}_3{}^{1a}$
3566·55	66·36	66·37	4	28031·71	$D_2{}^1-D_2{}^1$
24·69	24·53	24·54	10	364·40	$d_3{}^1-\bar{p}_2{}^1$
		19·78	1	402·81	$f_2{}^1-\bar{f}_2{}^{1a}$
	15·06	15·06	7	440·93	$d_2{}^1-f_3{}^{1a}$
	10·37	10·34	6	479·16	$\bar{d}_1{}^1-p_0{}^1$
	3500·87	3500·85	3	556·33	$f_3{}^1-d_2{}^1$

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
3493·13	3492·96	3492·97	8	620·73	$\bar{d}_2{}^1—\bar{p}_1{}^1$
	83·83	83·78	3	696·31	$f_2{}^1—d_1{}^1$
	72·56	72·55	5	789·10	$\bar{d}_2{}^1—d_3{}^1$
61·84	61·65	61·66	8	879·63	$\bar{d}_3{}^1—\bar{f}_4{}^1$
	58·45	58·47	8	906·29	$\bar{d}_1{}^1—\bar{f}_2{}^1a$
	52·87	52·89	5	952·97	$\bar{d}_2{}^1—\bar{f}_3{}^1$
	3446·26	3446·26	7	29008·65	$\bar{d}_2{}^1—d_2{}^1$
	37·31	37·28	4	084·44	$f_4{}^1—\bar{f}_4{}^1$
	33·60	33·57	5	115·92	$\bar{d}_3{}^1—\bar{f}_3{}^1a$
	23·73	23·71	4	199·71	$\bar{d}_1{}^1—d_1{}^1$
	14·77	14·77	10	276·17	$\bar{d}_3{}^1—\bar{f}_4{}^1a$
		13·94	2	283·27	$\bar{d}_2{}^1—\bar{f}_2{}^1$
	13·52	13·48		287·26	$f_3{}^1—\bar{f}_2{}^1a$
		09·58	0		$f_4{}^1—\bar{f}_3{}^1a$
3393·10	3392·96	3392·99	6	464·08	$\bar{d}_3{}^1—d_3{}^1$
	91·06	91·05	3	480·95	$f_4{}^1—\bar{f}_4{}^1a$
		89·36	1	495·68	
		86·95	0		
	80·57	80·58	7	572·29	$\bar{D}_2{}^1—\bar{P}_1{}^1$
	74·28	74·23	1	627·93	$\bar{d}_3{}^1—\bar{f}_3{}^1$
	72·05	72·00	1	647·55	
	69·57	69·58	7	668·83	$f_4{}^1—d_3{}^1$
	66·18	66·17	2	698·85	$f_3{}^1—\bar{F}_3{}^1$
		65·77		702·31	$\bar{D}_2{}^1—\bar{f}_3{}^2$
	61·61	61·56	2	739·6	$\bar{d}_2{}^1—\bar{f}_2{}^1a$
		37·02	0		$\bar{d}_3{}^1—f_2{}^1$
		28·72	0		$\bar{d}_2{}^1—d_1{}^1$
		22·32	1	30090·85	$\bar{D}_2{}^1—d_3{}^2$
	20·28	20·26	1	109·5	$f_3{}^1—D_2{}^1$
15·8	15·68	15·67	2	151·19	$\bar{d}_2{}^1—\bar{F}_3{}^1$
		3271·12	1		$\bar{d}_2{}^1—D_2{}^1$
		50·75	2	753·31	$D_2{}^1—d_2{}^2$
	3243·07	43·06	4	826·16	$\bar{d}_3{}^1—\bar{F}_3{}^1$
		34·66	1	906·31	
3233·05		33·17	1	920·5	
	32·93	32·95	5	922·66	
		26·99	1	979·69	
	25·06	25·03	2	998·53	$\bar{D}_2{}^1—d_1{}^2$
	21·68	21·66	2	31030·96	$f_4{}^1—\bar{F}_3{}^1$
3134·21	3134·09	3134·11	10	897·81	$\bar{d}_1{}^1—\bar{f}_2{}^2$
	14·14	14·13	1	32102·44	$d_2{}^1—\bar{P}_1{}^1$
		07·72	0	168·66	$f_3{}^1—d_3{}^2$
	05·48	05·47	1	191·97	$f_2{}^1—d_1{}^2$

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
3102·02	01·87	01·88	10	229·18	$\overline{D_2}^1—\overline{F_3}^2$
	01·55	01·56		232·48	$\overline{d_2}^1—\overline{f_3}^2$
	3099·13	3099·12	1	32257·92	
	97·15	97·57	1	274·05	
		97·12		278·72	$f_3^1—f_2^2$
3080·9	80·79	80·76	2	450·15	$\overline{d_1}^1—d_2^2$
		66·46	0	601·47	
64·76	64·63	64·63	2	620·95	$\overline{d_2}^1—d_3^2$
57·79	57·64	57·65	9	695·41	$\overline{d_1}^1—d_1^2$
54·46	54·3	54·32	7	731·06	$\overline{d_2}^1—\overline{f_2}^2$
50·99	50·8	50·83	10	768·49	$\overline{d_3}^1—\overline{f_4}^2$
		45·01	1	831·08	$f_3^1—d_2^2$
38·09	37·92	37·94	8	907·5	$\overline{d_3}^1—\overline{f_3}^2$
		31·87	1	973·38	$f_4^1—\overline{f_4}^2$
	19·16	19·15	3	33112·29	$f_4^1—\overline{f_3}^2$
12·14	11·99	12·01	8	190·81	$\overline{D_2}^1—D_2^2$
03·76	03·58	03·63	10	283·39	$\overline{d_2}^1—d_2^2$
02·65	02·46	02·49	10	295·98	$d_3^1—d_3^2$
	2994·46	2994·46	3	385·31	
	92·59	92·60	3	406·07	$\overline{d_3^1}—\overline{f_2^2}$
		84·13	1	500·87	$f_4^1—d_3^2$
	81·68	81·65	2	528·7	$\overline{d_2}^1—d_1^2$
	43·95	43·92	4	958·39	$\overline{d_3^1}—d_2^2$
		2821·30	3	35434·29	$\overline{d_3}^1—\overline{F_3}^2$
		2798·65	4	720·99	$\overline{d_2}^1—D_2^2$
		2511·02	2	39812·46	
		10·89		814·61	
		2491·184	1	40129·45	
		90·689		137·43	
		84·039	1	244·87	$\overline{D}_2^1—o_3^1$
		76·88	1	361·25	$f_4^1—a_3^1$
		72·24	2		
2455·6		—			
		41·83	4	940·45	$\overline{d_1}^1—k_2^1$
37·98		37·90	3	41006·47	
29·17		—			
16·21		—			
		2424·03		241·16	$\overline{d_1}^1—m_2^1$
		23·66	4	247·39	
		23·33		253·02	$f_3^1—c_4^1$
		2421·23	4	41288·76	$f_3^1—e_4^1$
		19·31	5	321·52	$f_3^1—k_2^1$
2412·36		12·65	3	435·65	$f_3^1—l_3^1$
		01·85	8	621·95	$f_3^1—m_2^1$

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
2396·74		2396·39	4	712·40	$f_2^1—u^1$
94·68		94·52	7	749·24	
		88·92	5	847·16	
87·87		87·56	4	871·05	$D_2^1—v^1$
		79·73	1		$\bar{D}_2^1—\bar{f}_2^3$
75·51		75·60	4	42081·77	
		75·43		084·83	
62·19		62·06	5	322·96	$f_3^1—o_3^1$
		60·64	5	348·48	$f_2^1—\bar{f}_3^3$
		58·87	5	380·3	$\bar{d}_3^1—c_4$
		56·87	5	416·18	$\bar{d}_3^1—e_4^1$
		55·06	5	42448·75	$\bar{d}_3^1—k_2^1$
	2347·47	—	—		
		46·64	6	601·23	$f_3^1—u^1$
		46·09	6	611·09	
45·48	45·47	45·55	6	621·04	$f_4^1—e_4^1$
41·80	—	—	—		
		38·5	9	749·4	$\bar{d}_3^1—m_2^1$
		37·82		761·84	$\bar{d}_1^1—t_2^1$
	37·52	37·49		767·90	$f_4^1—l_3^1$
	37·12	37·10		775·05	$\bar{d}_2^1—o_3^1$
34·68	—	—			
		31·70	3	873·98	$f_3^1—q_3^1$
	30·02	29·97	9	905·80	
25·91	25·82	25·80		982·77	$f_3^1—r^1$
		21·96	9	43053·93	$\bar{d}_3^1—\bar{f}_4^3$
	21·47	21·39		064·49	$f_2^1—v^1$
	20·11	20·03		089·60	$f_4^1—n_5^1$
18·60	18·80	18·78	9	112·91	
	17·14	17·16	9	143·06	$f_3^1—t_2^1$
		13·98	9	202·27	
	13·64	13·66		208·36	
12·50	12·35	12·34		232·99	$f_3^1—\bar{f}_3^3$
	11·01	10·96		258·81	$f_4^1—\bar{f}_4^3$
		2308·16	2	43311·19	
		07·35	2	326·37	$\bar{d}_2^1—q_3^1$
		06·42	2	343·90	
2302·56		02·97	4	408·75	
		01·57	10	435·25	$\bar{d}_2^1—r^1$
		00·77		450·24	$\bar{d}_3^1—o_3^1$
2296·66		2296·55	5	530·19	
		93·85	10	581·43	$d_2^1—t_2^1$
	2293·18	93·11		595·36	
	90·05	—	—	—	

TABLE OF ABSORBED WAVE-LENGTHS.—*Continued.*

Buffam and Ireton (under-water spark).	McLennan and McLay (vacuum furnace).	Authors.			Series Notation (Bechert and Sommer).
		Wave-length.	Int. (abs.).	ν (vac.).	
75·79		75·57	1	931·41	
		74·65	2	949·14	f_3^1—v^1
		71·94	3	44001·62	$\bar{a}_3^1$—q_3^1
		70·21	2	035·21	
		67·55	5	086·8	f_3^1—f_2^3
		66·40	5	109·15	
64·57	—	—	—	—	
		61·40	6	206·46	f_4^1—q_3^1
		59·55	6	242·87	
58 2	—	58·13	6	270·62	d_3^1—t_2^1
		54·80	1	336·09	
		53·83	6	355·10	d_3^1—f_3^3
		53·55	5	360·68	
53·0	—	—	—	—	
		51·47	4	401·67	$\bar{a}_2^1$—v^1
47·3	—	—	—	—	
	44·53	44·50	8	540·21	$\bar{d}_2^1$—$\bar{f}_2^3$
		30·93	2	810·35	
26·41	—	—	—	—	
		24·84	2	933·09	
		22·93	2	971·58	
	21·83	21·92	3	992·06	
		(2217·82)	4	45075·24	
16·52		16·46	4	102·93	
11·16		11·27	3	208·81	
		11·02	3	213·86	
		(2205·59)	1	325·15	
01·52		01·53	4	408·75	
		(2200·72)	4	425·45	
		2197·31	8	495·99	
2191·04	—	—	—	—	
		2190·18	2	644·05	
		2188*	8	45704·0	
		2186*	8	45731·0	
		2183*	6	45793·0	
2175·22	—	75·10	5	960·5	
		69·10	5	46008·6	
61·31	—	61·25	5	255·0	
59·83		59·80	5	286·1	
		57·84	3	328·0	
		2154*	7	46412·0	
		2142*	6	46670·0	
38·69		—	—	—	
		31·28	5	47013·5	
25·98		2126*		47022·0	
		24·84	3	047·6	
		21·4	2	123·8	

Wave-lengths marked * are probably unresolved lines clustered together into a broad band.

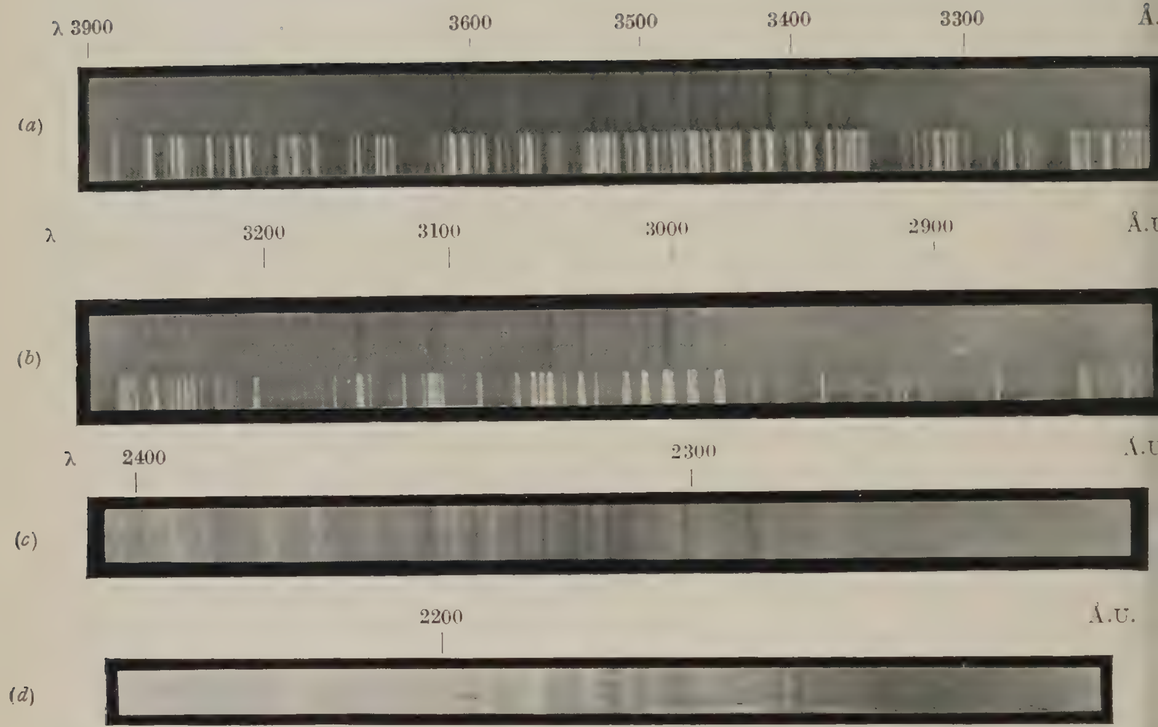

FIG. 2.—UNDER-WATER SPARK ABSORPTION SPECTRUM of NICKEL.

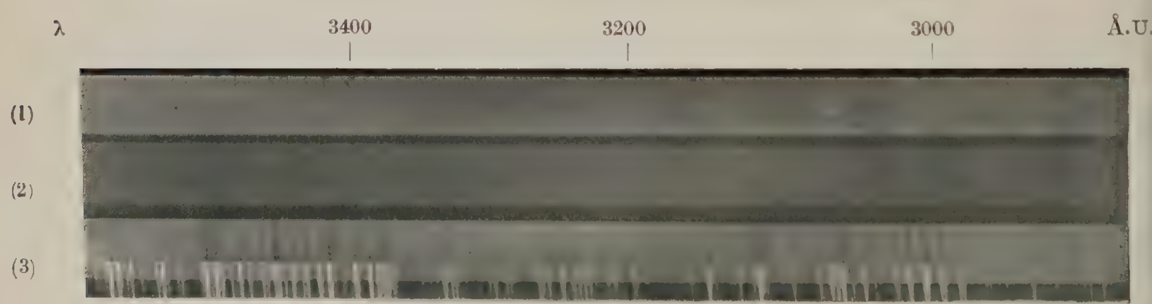

FIG. 3.—UNDER-WATER SPARK SPECTRUM of NICKEL.

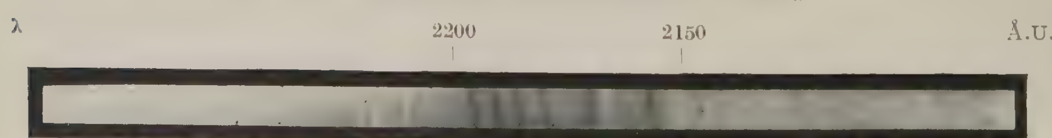

FIG. 4.—UNDER-WATER SPARK SPECTRUM of IRON.

[*To face page* 361.

A careful examination of the table shows that lines of multiplets having d^1's as initial orbits were obtained mostly as absorption lines. Furthermore, the results show that the intensity rule and the selection rule for the inner quantum numbers are accurately fulfilled. The presence of some absorption lines also indicates that the selection rule for azimuthal quantum numbers, however, breaks down. These may be ascribed to the strong electric and magnetic fields at the spark gap. Notable among these are the (f, f), (d, d), (d, D) combinations. It will also be found that wavelengths with u, v, t, o as the final level were mostly absorbed, while those with a and b as final levels were not absorbed.

Bechert and Sommer classified only lines up to λ2240. Of the 150 lines obtained in absorption by us in this region, 112 were classified by these authors. Between λ2240 and λ2100, 25 wavelengths were absorbed, many of these being intense in absorption, thereby showing that these also belong to some fundamental combinations. These experiments confirm in a striking manner the classification of Bechert and Sommer, though at the same time it must be remarked that many lines with the f term as the initial level were not obtained as absorption lines.

Fig. 3 shows the absorption spectrum of nickel from λ3600 to λ2900 under different conditions of excitation, which conclusively indicates that with proper arrangement the under-water spark can be made use of as an efficient means to the study of the absorption and series spectra of different elements, particularly those with high boiling points.

Note on Fe Spectrum.

The arc spectrum of nickel is exactly similar to that of iron, which consists of triplets, quintets and septets, with intercombinations among the different systems. The under-water absorption spectrum of this element was found to consist of some very strong lines in the region λ2300-λ2100 which were not included in Laporte's[12] scheme. The following table gives the wave-lengths of these lines.

Table of Absorbed Wave-lengths (Fe).

λ	Int.	λ	Int.
2191·95	10	2162·10	
91·2		61·69	
87·29	10	61·28	
86·90		60·23	
86·49		56·91	
81·60	10	55·95	10
80·92		55·78	
78·14	10	55·14	
76·92		50·66	
66·92	10	50·26	
66·68		48·57	
		47·84	
		47·14	
		44·57	
		41·83	
		31·04	

As was already indicated, the under-water spark spectrum of Fe exhibited some emission lines belonging to the first spark spectrum of iron, prominent among these being the lines of the *DP* multiplet of the quartet system of Fe^{+}.

MULTIPLET IN THE SPECTRUM OF Fe^{+}.

	D_4^4	436·51	D_3^4	288·50	D_2^4	166·23	D_1^4
P_3^4	5 2562·541 39011·94		4 2591·549 38575·43		2 2611·08 38286·91		—
422·3							
P_2^4	—		4 2563·484 38997·73		4 2582·590 38709·24		1 2593·528 38543·03
236·34							
P_1^4	—		—		3 2566·916 38945·6		3 2577·92 38779·35

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XXXVI.—THE INFLUENCE OF ELECTROLYTES IN ELECTRO-ENDOSMOSIS.

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(*Communicated by* Prof. A. GRIFFITHS.)

ABSTRACT.

This Paper gives the results of electro-endosmotic determinations with certain aqueous solutions of electrolytes in glass diaphragms, and values are obtained for the interfacial potential of the Helmholtz electrical double layer. The dependence of the conductivity on the electro-endosmotic flow has been investigated by measurements of the current flowing through the diaphragm during each determination, and the data used to trace the variations in the thickness and the charge of the electrical double layer by the application of a formula derived by Smoluchowski.

INTRODUCTION.

NUMEROUS researches have been undertaken in recent years on electro-endosmosis, cataphoresis, and stream potentials with aqueous solutions of electrolytes against solids (and certain oils), which become negatively charged in pure water. The results have usually been given in terms of the potential ζ of the electrical double layer, which, according to the Helmholtz theory, is set up at the interface solid (or oil)-aqueous solution. A general conclusion to be drawn from these results, as Freundlich* has observed, is that with most electrolytes with univalent, inorganic cations, ζ increases initially with the concentration, attains a maximum value, and then strongly and rsgularly decreases.

The data for the interface glass-aqueous solution, however, is not altogether in harmony with this conclusion. Kruyt† investigated the stream potentials produced by pumping aqueous solutions of hydrochloric acid, potassium chloride, and barium chloride through glass capillaries, and obtained pronounced maxima in the ζ-concentration curves in all the cases mentioned, including that of barium chloride. On the other hand, Elissafoff‡ and Powis§ in electro-endosmotic measurements with aqueous solutions of sodium chloride (Elissafoff), potassium chloride (Powis), and barium chloride (Elissafoff and Powis) against glass, found that increase in the electrolyte concentration, with the most dilute solutions, produced a decrease in the value of ζ. Kruyt† has questioned the method used in the calculation of Elissafoff's results, but without being able to reconcile the data for glass capillaries with his own results.

The present work, consisting of direct electro-endosmotic measurements with aqueous solutions in glass diaphragms, is devoted to the study of the phenomenon at low electrolyte concentrations, with special reference to the production of maxima in the ζ-concentration curves. At the same time, the dependence of the conductivity on the electro-endosmotic flow has been investigated, and the data used to trace the variations in the thickness and the charge of the electrical double layer by the application of a formula derived by Smoluchowski.||

* "Kapillarchemie," p. 351 (1922).

† Koll. Zeit., 22, 81 (1918); *see* also Freundlich and Rona, Sitz. d. Preusz. Akad. d. Wiss, 20, 397 (1920).

‡ Zeit. Phys. Chem., 79, 385 (1912).

§ Ibid., 89, 91 (1915).

|| Anz. Akad. Wiss Krakau, A, 182 (1903).

The Apparatus.

The apparatus employed, the main parts of which were made from hard glass tubing, was similar in construction to that used by Briggs, Bennett and Pierson* but it was found desirable to adopt a different arrangement of electrodes, and a somewhat different mode of procedure.

The horizontal electrolyzing chamber A, A' (Fig. 1), with vertical side arms S, S', was enlarged slightly between D and D', to form a chamber in which the porous diaphragm was built up. The side arms S, S' were fitted with grooved corks, which carried the electrodes E, E'. Attached to the horizontal chamber by ground glass joints were the three-way taps T, T', which, in turn, were connected, by means of short rubber connexions, to the bent tube BHB' of uniform bore. The speed and direction of flow through the diaphragm were measured by the movement of a small air bubble (H), introduced into the tube BHB' by manipulation of the taps T, T'.

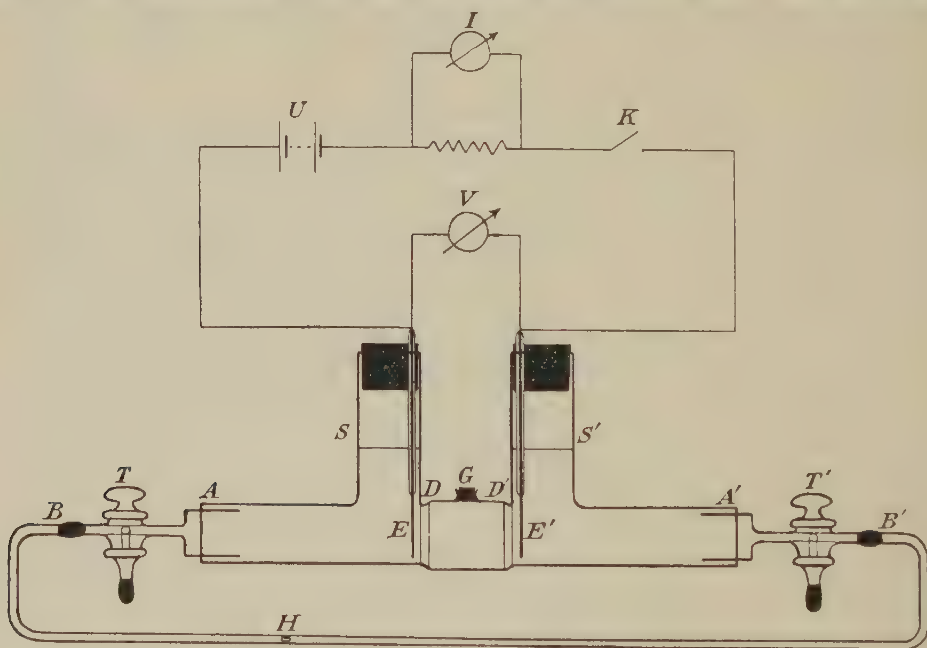

Fig. 1.—The Apparatus.

The capacity of the tube BHB' was determined as follows :—

Connexion was made with the chamber AA' at T, and liquid delivered from the tube in drops at the tap T'. The liquid delivered from T' while the bubble moved over 25 cm. of the tube was collected and weighed, the results of several determinations giving the capacity of the tube as 1·836 c.c. per 25 cm. length.

Pure vaseline was employed as a lubricant for the taps and joints, and the outsides were smeared with a mixture of vaseline and paraffin wax ; the taps, in addition, were fitted with small rubber stoppers during the determinations of liquid flow.

* Jour. Phys. Chem., 22, 256 (1918).

The Diaphragm.

The diaphragm material, in the form of a 200 mesh powder, consisted of an easily fusible glass, similar to that constituting the capillaries used in the stream potential experiments of Freundlich and Rona.* After careful grading, the powder was heated first with strong hydrochloric acid; then, after washing with distilled water, with chromo-sulphuric acid; and finally washed thoroughly with distilled water. The purified glass was kept sealed under distilled water.

Immediately before building up each diaphragm a suitable quantity of the purified powder was placed in a U-tube with distilled water, and 200 volts applied between the electrodes in the limbs; this operation was repeated with changes of water until no further electrolysis could be detected. The electrolyzing chamber $A\ A'$ was then fixed in a vertical position, and the diaphragm built up in the section $D\ D'$ on a perforated cork, upon which was placed a compact plug of glass wool, which had previously been treated in the same manner as the glass powder. The glass powder, suspended in distilled water, was poured on to the plug, and the water drawn through with the aid of a filter pump. Finally, the diaphragm was completed by adding an upper plug of glass wool. Guiding lines 5 cm. apart were provided at D and D', so that each diaphragm, including plugs, could be constructed of this length.

The Electrodes.

A silver anode and a silver chloride cathode, prepared after the manner recommended by Washburn,† were employed. For the anode, about 35 cm. of silver wire 1 mm. in diameter was cemented into a thin glass tube. The protruding length, constituting the greater part of the wire, was wound into the form of a flat spiral and plunged into warm dilute nitric acid until violently attacked; washed with boiling distilled water, and then with alcohol, the excess of which was finally removed by the application of heat. The tube carrying the electrode was then fixed in the grooved cork of the side arm S' of the apparatus, so as to bring the plane of the spiral normal to the axis of the electrolyzing chamber $A\ A'$. A similar spiral of silver wire, upon which a layer of granular silver chloride had been deposited electrically from a molar solution of sodium chloride, was employed as cathode, and suspended in the side arm S of the apparatus. With electrodes of this type it was found possible to obtain results at much lower voltages than were applied by Briggs, Bennett and Pierson.‡

The current meter I, fitted with a variable shunt so as to obtain a wide range, and the battery of storage cells U, were placed in series with the electrodes through the key K, and the high-resistance voltmeter V placed across the electrodes. In determining the current through the diaphragm, adjustment was made in respect of the current (generally small in relation to the main current) through the voltmeter.

Experimental.

A separate diaphragm was prepared for each solution studied, but the same quantity of purified glass powder was used in each case, and each diaphragm built up under similar conditions. In addition, new electrodes were prepared for use with each diaphragm. The special method employed for washing out the diaphragm permitted the use of the same diaphragm for different concentrations of a particular solution.

Before building up each diaphragm, the whole apparatus was thoroughly washed

* Loc. cit.

† Jour. Am. Chem. Soc., 31, 322 (1909).

‡ Loc. cit.

out with hot chromo-sulphuric acid to remove grease and other impurities. Traces of impurities in the tube *BHB'* were found to impede the progress of the air bubble index ; but this trouble was entirely removed by the cleansing treatment with chromo-sulphuric acid.

Determinations of the flow were made first with conductivity water, and then with the particular solution in increasing concentration up to 0·005 molar.

The method adopted for washing out the diaphragm was as follows :—

The bubble tube *B'HB* was cut off from the electrolyzing chamber by means of the taps *T*, *T'*, and the chamber emptied of liquid. The solution of next higher concentration was then introduced with a head of liquid in the side tube *S*. Under the influence of the hydrostatic pressure the solution flowed through the diaphragm into the right-hand part of the chamber, the flow being maintained by drawing solution from the tap *T'* at convenient intervals, and adding to the solution in the side arm *S*. After a considerable amount of solution had flowed through the diaphragm the chamber was emptied, and the operation repeated with a head of liquid in the side arm *S'*. After four such washings, with liquid heads alternately in each side arm, the liquid in the tube *BHB'* was siphoned out and replaced by conductivity water, and a small air bubble introduced by manipulation of the taps *T*, *T'*. Control experiments showed that similar washings, with a further quantity of solution, produced no appreciable alteration in the results.

After the apparatus had been allowed to stand for about thirty minutes, the tube *BHB'* was connected with the chamber *AA'*, and the bubble timed over 5 cm. of the tube with the aid of a stop watch, readings of current and applied potential difference being taken at the same time.

The temperature of the room in which the work was undertaken was maintained as far as possible constant at 18°C., determinations being made when the solution in the apparatus attained this temperature. Control experiments, with a thermometer in the side tube *G* of the chamber *AA'*, showed that there was no appreciable temperature rise in the diaphragm during each determination.

Results.

(*a*) *Preliminary.*

Table I gives the results of a series of measurements with conductivity water at various applied potentials.

Table I.

V	T	$I/TV \times 10^4$
8·24	299·0	4·06
12·34	200·8	4·04
16·48	150·4	4·03
20·62	119·7	4·05
Volts	Secs.	

V is the potential difference applied at the electrodes, and *T* the time of flow over 5 cm. of the bubble tube. It will be seen from column 3 that the values give an accurate linear relation between the electro-endosmotic flow (proportional to I/T), and the total fall in potential through the diaphragm (proportional in this case to the applied potential) in agreement with previous experimental work* and with the theory of Helmholtz and others.†

* *See* the historical account by T. R. Briggs, Jour. Phys. Chem., 21, 198 (1917).
† *See* part (*b*) of this Section.

Table II, relating to solutions of potassium chloride, records the results of experiments designed to give the relation between the applied potential difference and the total fall in potential through the diaphragm.

TABLE II.

c	V	I_e	T	$I_e/TV \times 10^3$
0·0002	8·12	5·40	93·0	7·15
	8·12	5·60	97·0	7·11
	8·12	5·80	99·6	7·17
0·002	8·12	5·40	60·4	11·01
	8·12	5·60	62·5	11·04
	8·12	5·80	65·2	10·96
Mols. per litre	Volts	Cm.	Secs.	

For this purpose the electrodes were set with the aid of a travelling microscope at effective distances of 2, 3 and 4 mm. respectively, from the extremities of the diaphragm, allowance being made for the thickness of the wire constituting the electrodes; and the applied voltage (V), time of flow (T) over 5 cm. of the bubble tube, and the distance (I_e) between the electrodes, taken in each case. It will be observed from column 5 that the values of I_e/TV are practically the same, at a given concentration (c in Table), for all three positions of the electrodes. Since the electro-endosmotic flow, at a given concentration, is proportional to the potential gradient in the diaphragm, it appears from this result that the total fall in potential (E) through the diaphragm, when the electrodes are placed close to its extremities, is given, within a fraction of 1 per cent., by VI_d/I_e, where I_d is the length of the diaphragm.

In order to test whether placing the electrodes close to the ends of the diaphragm introduced disturbances in the flow and the current by reason of concentration changes about the electrodes, a series of observations was carried out with potassium chloride solutions over the concentration range 0·0002 molar to 0·005 molar, with the electrodes at an effective distance of 4 mm. from the extremities of the diaphragm. In each case the bubble was timed over a section of the tube, allowed to run over the next section, and then timed over the third section.

TABLE III.

c	E	T	I
0·0	7·17	296·5	84
	7·17	295·1	80
0·0002	7·17	96·3	282
	7·17	96·8	291
0·0005	7·17	68·0	497
	7·17	66·8	493
0·0007	7·17	59·1	677
	7·17	59·4	677
0·001	7·17	57·2	867
	7·17	56·8	875
0·002	7·17	62·9	1,420
	7·17	61·7	1,420
0·005	7·17	223·6*	3,090
	7·17	214·8*	3,090
Mols. per litre.	Volts.	Secs.	Micro-amperes.

* Bubble timed over 2½ cm. only of the tube.

The results are given in Table III, and show that the variation in the time of flow for each pair of observations was generally under 1 per cent. with concentrations up to 0·001 molar, about 2 per cent. for 0·002 molar, and about 4 per cent. for 0·005 molar, the current (*I* in Table, column 4) in each case remaining remarkably steady. Compared with the results of previous investigators, these differences are not very considerable, but the final observations in the present work (*see* Table IV) were each repeated after washing out the diaphragm with fresh solution.

(*b*) *Determinations of Interfacial Potential.*

Table IV and the graphs of Fig. 2 give the results for aqueous solutions of potassium chloride, barium chloride and hydrochloric acid.

TABLE IV.

(1) Potassium chloride.					(3) Hydrochloric acid (with conductivity water).				
c	E	T	ζ	Mean ζ	c	E	T	ζ	Mean ζ
0·0	7·17	303·5	0·048		0·0	7·17	299·3	0·049	
	7·17	299·9	0·048	0·048		7·17	297·4	0·049	0·049
0·0002	7·17	96·9	0·150		0·0002	7·17	86·5	0·169	
	7·17	98·1	0·148	0·149		7·17	87·4	0·167	0·168
0·0005	7·17	68·8	0·211		0·0005	7·17	60·1	0·243	
	7·17	68·2	0·213	0·212		7·17	59·7	0·245	0·244
0·0007	7·17	60·7	0·239		0·0007	7·10	54·7	0·270	
	7·17	60·1	0·242	0·241		7·10	55·1	0·268	0·269
0·001	7·17	57·9	0·251		0·001	7·10	54·3	0·272	
	7·17	57·9	0·251	0·251		7·10	54·7	0·270	0·271
0·002	7·17	63·9	0·228		0·002	7·10	72·7	0·203	
	7·17	63·3	0·230	0·229		7·10	72·2	0·205	0·204
0·005	7·17	223·8*	0·065		0·005	7·10	249·4*	0·059	
	7·17	224·6*	0·065	0·065		7·10	251·2*	0·059	0·059

(2) Barium chloride.					(4) Hydrochloric acid (with distilled water).				
c	E	T	ζ	Mean ζ	c	E	T	ζ	Mean ζ
0·0	7·10	294·0	0·050		0·0	7·10	86·7	0·169	
	7·10	295·9	0·050	0·050		7·10	85·8	0·171	0·170
0·0002	7·10	115·6	0·128		0·0002	7·10	65·4	0·225	
	7·10	114·5	0·129	0·128		7·10	66·0	0·223	0·224
0·0005	7·10	103·0	0·143		0·0005	7·10	60·0	0·245	
	7·10	103·3	0·143	0·143		7·10	59·5	0·247	0·246
0·0007	7·10	106·7	0·138		0·0007	7·10	54·9	0·268	
	7·10	105·8	0·139	0·139		7·10	54·6	0·269	0·268
0·001	7·10	118·5	0·124		0·001	7·10	54·3	0·270	
	7·10	119·2	0·124	0·124		7·10	54·5	0·270	0·270
0·002	7·10	163·1	0·090		0·002	7·10	72·6	0·202	
	7·10	164·7	0·090	0·090		7·10	72·1	0·204	0·203
0·005	7·10	459·8*	0·032		0·005	7·10	251·8*	0·058	
	7·10	462·4*	0·032	0·032		7·10	252·6*	0·058	0·058
Mols. per litre.	Volts.	Secs.	Volts.	Volts.	Mols. per litre.	Volts.	Secs.	Volts.	Volts.

* Bubble timed over 2½ cm. only of the tube.

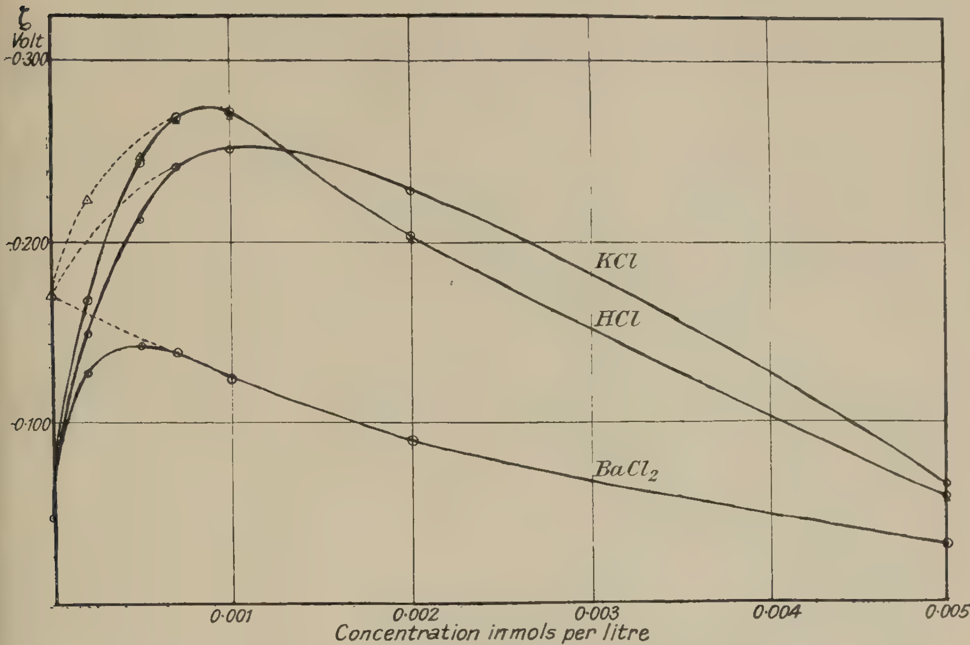

FIG. 2.—VARIATION IN THE POTENTIAL OF THE DOUBLE LAYER.

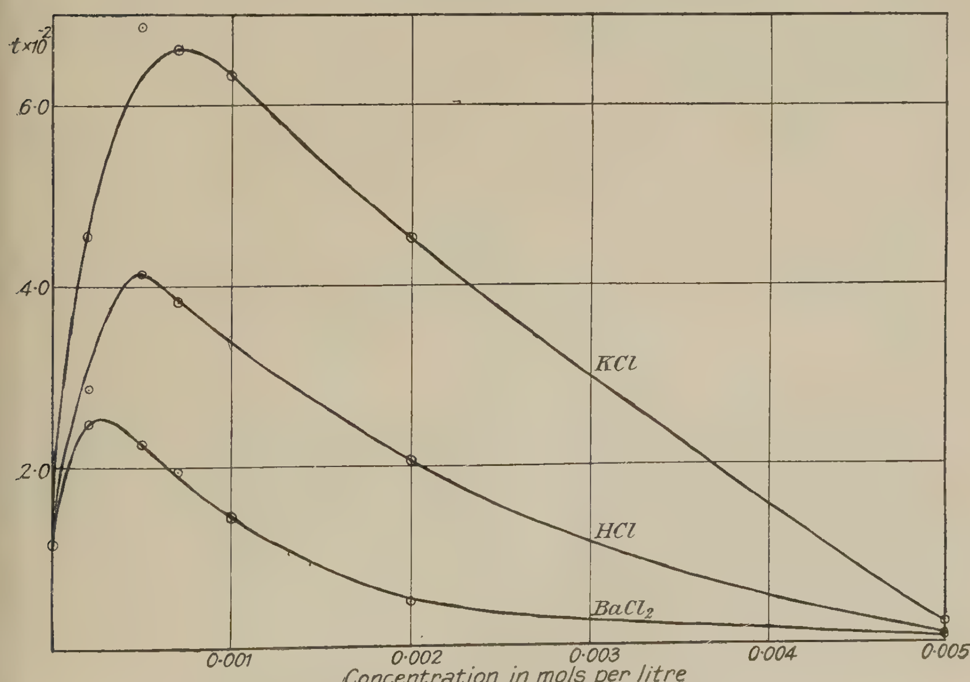

FIG. 3.—VARIATION IN THE THICKNESS OF THE DOUBLE LAYER.

ζ (column 5, Table IV.) is the potential of the electrical double layer at the interface glass-aqueous solution, calculated from the formula

$$v=q\zeta ED/4\pi\eta I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where v is the amount of liquid transported in unit time through the diaphragm, E the total fall in potential through the diaphragm, D the dielectric constant, η the viscosity coefficient of the liquid, and q and I respectively the effective cross-section and length of the diaphragm. ζ is negative in sign throughout.

Smoluchowski* has shown mathematically that expression (1), which is similar in form to that derived by Helmholtz† for a single capillary, is valid for the case of a porous diaphragm. The expression differs from that of Helmholtz, however, in containing the dielectric constant D. The inclusion of this factor follows the modern view‡ that the two layers forming the double layer do not lie, as assumed by Helmholtz, at a distance of one molecular diameter from one another, but extend much more deeply into the liquid. Gouy§ has shown that a diffuse double layer of this character may be replaced by two parallel sheets of charge—i.e., by a double layer of the form conceived by Helmholtz. The values calculated by Gouy (e.g., $9{\cdot}6\mu\mu$ for 0·001 molar solution) for the thickness of this equivalent, Helmholtz double layer are quite small in relation to the radius of a capillary of 0·05 mm. bore, which is roughly equivalent to a single channel in the present diaphragms, so that the condition imposed by Helmholtz, in deriving the expression for ζ, that the thickness of the double layer should be negligible in comparison with the dimensions of the cross section of the tube, may still be regarded as satisfied.

The values for q/I (*see* Table V) were obtained by means of a method due to Fairbrother and Mastin.‖

TABLE V.

$N/10$	$\lambda \times 10^3$	E	$I \times 10^3$	q/I $(I/\lambda E)$	Mean q/I
KCl	11·20	7·17	42·34	0·527	
		3·59	21·12	0·525	0·526
$BaCl_2$	9·08	7·10	33·80	0·524	
		3·55	16·88	0·524	0·524
HCl_A	35·14	3·55	65·4	0·524	
		3·55	65·1	0·522	0·523
HCl_B	35·14	3·55	65·6	0·526	
		3·55	65·6	0·526	0·526
	Recip. Ohms.	Volts.	Amps.		

Each series of observations was concluded with a determination using $N/10$ solution. No perceptible liquid transport was observed at this concentration, but readings of the current and applied potential difference were taken as before. No electro-endosmotic flow being observed, the surface conductivity in $N/10$ solution (*see* part (*c*) of this Section) was assumed to be negligible in relation to the bulk conductivity; consequently, with current I, total fall in potential through the diaphragm E,

* Loc. cit.
† Wied. Ann., 7, 337 (1879).
‡ *See* Freundlich, "Kapillarchemie," pp. 342-3 (1922).
§ Jour. d. Phys. (4), 9, 457 (1910).
‖ Jour. Chem. Soc., 125, 2319 (1924).

and q and I respectively, the effective cross-section and length of the diaphragm, the following relation obtained,

$$I = E\lambda q/I \text{ or } q/I = I/\lambda E,$$

λ being the specific conductivity of the solution employed. The values of λ were obtained mainly from the data of Kohlrausch.*

With the extremely dilute solutions of the present work, the dielectric constant and the viscosity coefficient are practically the same as for pure water, and the values 80 and 0·01057, relating respectively to the dielectric constant and the viscosity coefficient of pure water, have been used throughout in applying the formula for ζ.

The results of sections (1) to (3) of Table IV refer to solutions made up with freshly-prepared conductivity water of specific conductivity approx. 10^{-6} recip. ohms. Section (4) of Table IV gives a series of results with solutions of hydrochloric acid prepared with laboratory distilled water (specific conductivity approx. 8×10^{-6} recip. ohms).

(*c*) *Dependence of the Conductivity on the Electro-endosmotic Flow and Variation in the Thickness of the Electrical Double Layer.*

The results are given in Table VI.

TABLE VI.

	c	$\lambda \times 10^5$	I	i_q $(E\lambda q/I)$	i_w $(I - i_q)$	i_w/i_q	$t \times 10^{-2}$	$\zeta/t \times 10^4$
(1) Potassium Chloride	0·0	0·10	78·8	3·8	75·0	19·7	1·17	4·09
	0·0002	2·57	281·2	96·9	184·3	1·902	4·55	3·28
	0·0005	6·40	487·2	241·4	245·8	1·018	6·88	3·07
	0·0007	8·94	668	337	331	0·982	6·62	3·64
	0·001	12·73	856	480	376	0·783	6·32	3·97
	0·002	25·25	1,389	952	437	0·459	4·52	5·06
	0·005	62·17	3,058	2,345	713	0·303	0·22	29·0
(2) Barium Chloride	0·0	0·10	75·8	3·7	72·1	19·5	1·28	3·90
	0·0002	4·70	419·6	174·9	244·7	1·399	2·49	5·14
	0·0005	11·56	768	430	338	0·786	2·25	6·35
	0·0007	16·13	966	600	366	0·610	1·96	7·08
	0·001	23·10	1,257	859	398	0·463	1·44	8·63
	0·002	44·84	2,268	1,668	600	0·360	0·50	17·9
	0·005	106·7	4,546	3,970	576	0·145	0·07	48·4
(3) Hydro-chloric acid	0·0	0·10	79·8	3·8	76·0	20·0	1·20	4·07
	0·0002	7·56	651·6	283·5	368·1	1·298	2·87	5·84
	0·0005	18·85	1,244	707	537	0·760	4·16	5·87
	0·0007	26·36	1,683	979	704	0·719	3·82	7·05
	0·001	37·59	2,008	1,396	612	0·438	4·46	
							3·40†	7·97
	0·002	75·06	3,537	2,787	750	0·270	2·05	9·94
	0·005	186·3	8,170	6,918	1,252	0·181	0·10	57·1
	Mols. per litre	Recip. Ohms.	Micro-amperes					

* *See* Noyes and Falk, Jour. Am. Chem. Soc., 34, 454 (1912).

† Interpolated value from the graph in Fig. 3.

In column 3 of the Table the mean total current (I) flowing through the diaphragm, as measured during each determination of electro-endosmotic flow, is given, and in column 4, the voltaic current (i_q), calculated from the expression $E\lambda q/I$, the letters having the significance indicated in the previous section.

In order to verify that this expression for the voltaic current could be applied in the present work, control experiments were carried out to ascertain (1) whether the electrolyte concentration in the diaphragm differed materially from the bulk concentration, by reason of adsorption phenomena attending the formation of the electrical double layer, and (2) whether the movement of the solution in the diaphragm altered the voltaic current.

To test the first point, a quantity of the purified glass powder was carefully dried, placed in a bottle, and 0·0002 molar potassium chloride solution added to fill the bottle. The bottle was then sealed and agitated vigorously to bring the whole of the solution into contact with the powder. After the bottle had been allowed to stand for about thirty minutes, the supernatant liquid was decanted off, a further quantity of solution added, and the operation repeated. Finally, after three such washings, the contents of the bottle were carefully filtered through glass wool to remove suspended glass particles, and the conductivity of the filtrate determined. Before proceeding to the filtration, a quantity of the original solution was poured

FIG. 4.—DETERMINATION OF CONDUCTIVITY WITH SOLUTION FLOWING PAST THE ELECTRODES.

through the filter, so as to minimise the possibility of adsorption of the solute taking place during the filtration. The results obtained were found to agree (within 1-2 per cent.) with concurrent determinations of the conductivity of the original solution, and also with the value given by the data of Kohlrausch. A further quantity of the dried powder was then taken, and the shaking process repeated with several washings of 0·002 molar potassium chloride solution. Conductivity measurements with the filtrate in the latter case gave similar agreement with the results for the original 0·002 molar solution. These results indicate that the final equilibrium concentration in the diaphragm, after several washings with a particular solution, was practically the same as the bulk concentration.

To test the second point, the original apparatus was employed with the bubble tube cut off from the chamber AA'. The electrodes were fixed in the vertical side arm S of the apparatus with the spirals one above the other, after the manner of the electrodes in a conductivity cell (Fig. 4). The current was first measured with the solution in the two side arms S, S' at the same level, the solution between the electrodes consequently remaining at rest. Solution was then withdrawn from the side arm S' by means of the tap T', giving a head of liquid in the arm S, which produced a flow through the diaphragm and movement of the solution between the

electrodes. The head of liquid in the arm S was arranged so that the average rate of flow past the electrodes was of the same order as the flow through the diaphragm in the electro-endosmotic determinations described in the previous section. Within a fraction of 1 per cent. no alteration in the current was observed. It appears from this result that the voltaic current through the diaphragm in the electro-endosmotic determinations, was not perceptibly different from that which would have been obtained if the solution had been at rest.

Values of the surface current (i_w), given by ($I - i_q$) are scheduled in column 5 of Table VI, and values of i_w/i_q in column 6.

In column 7 of the table, values are given of the expression $\frac{\zeta^2}{\lambda i_w/i_q} \times 10^{-2}$, which, as indicated by an expression derived by Smoluchowski* is proportional to the thickness of the electrical double layer. The values of ζ are taken from Table IV.

Smoluchowski's formula relates to the case of a single capillary, and is as follows,

$$\frac{i_w}{i_q} = \frac{\omega}{q\eta\delta\lambda}\left(\frac{\zeta D}{4\pi}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

ω is the circumference of the tube, δ the thickness of the electrical double layer, and the other letters have the significance indicated in the previous section. This expression, suitably modified as regards the constants q and ω, has been used in connexion with the work of Stock† on powdered quartz. In the range of electrolyte concentration of the present work the expression reduces to the form $i_w/i_q = \zeta^2/\delta\lambda \times$ (a constant), giving δ proportional to $\frac{\zeta^2}{\lambda i_w/i_q}$, the expression t of column 7 of Table VI. The variation of t with the concentration is shown graphically in Fig. 3.

Discussion of Results.

The curves of Fig. 2 show that the potential of the interface glass-aqueous solution increased initially with the concentration, attained a maximum value, and then regularly decreased with solutions of potassium chloride, barium chloride and hydrochloric acid, in agreement with Kruyt's general result. The curves are similar in shape to those of Kruyt, and in the same relative positions; but the values of ζ are generally greater than those obtained by him, and the maxima occur at higher concentrations—e.g., maximum value of ζ in the present work with potassium chloride solutions $-0{\cdot}251$ volts at a concentration of 0·001 molar, and in Kruyt's work $-0{\cdot}086$ volts at 0·0003 molar. In making the comparison, it should be observed that Kruyt calculated the values of ζ in absolute units from the original stream potential formula of Helmholtz‡ and the values given in his Paper consequently require to be multiplied by 300/80 to obtain ζ in volts and to correct for the dielectric constant.

The values of ζ for the interface glass-pure water are in good agreement with those obtained from the results of the experiments of Quincke and Tereschin§

* Loc. cit.

† Anz. Akad. Wiss. Krakau, A, 635 (1912); and *see* Freundlich, "Kapillarchemie," p. 338 (1922).

‡ Loc. cit.

§ *See* Freundlich, "Kapillarchemie," p. 330 (1922).

on the rise of liquid in capillary tubes under the influence of an applied potential; the values also fall between those ($-0{\cdot}035$ and $-0{\cdot}089$ volts respectively) given by the data of Kruyt and Powis (loc. cit.).

The importance of employing water of a high degree of purity in electro-endosmotic determinations is shown from the results of sections (3) and (4) of Table IV. The value of ζ with distilled water (specific conductivity 8×10^{-6} recip. ohms) is $-0{\cdot}170$ volts, against $-0{\cdot}049$ volts with conductivity water (specific conductivity 10^{-6} recip. ohms); the values of ζ for the distilled water solutions of hydrochloric acid are similarly greater than those for the conductivity water solutions, as indicated by the dotted curve in Fig. 2; above 0·0007 molar concentration, however, the results with distilled water and conductivity water practically coincide. A parallel to this result is given by the work of Alty* on the cataphoresis of gas bubbles in water. Alty found that the velocity of cataphoresis increased with the conductivity of the water to a maximum value in water of specific conductivity $8{\cdot}5\times10^{-6}$ recip. ohms. The dotted curves in Fig. 2 for solutions of potassium chloride and barium chloride are obtained by taking the value of ζ at zero concentration as $-0{\cdot}170$ volts, and combining this result with the values for conductivity water solutions of concentration greater than 0·0007 molar. It will be seen that the maximum with barium chloride disappears entirely.

The results of Table VI, columns 3-6, given graphically in Fig. 5, are in agreement with the conclusions of Smoluchowski, from theoretical considerations, that electro-endosmosis must increase the ordinary galvanic conductivity in consequence of the surface current produced. The values given in column 6 for the ratio of the surface current to the voltaic current show that the surface current with pure water was practically twenty times as great as the voltaic current. The values for the solutions are much smaller, the greatest being 1·902 (with 0·0002 molar potassium chloride), and decrease with rising concentration. In previous work on this subject,† conductivity cells have apparently been used, with the space between the electrodes filled with the diaphragm material and the experimental liquid; and the conductivity determined by the usual alternating-current method of Kohlrausch. Stock observed the phenomenon with several organic liquids in quartz powders, and found that the current strength, with the finest quartz particles, increased to approximately twenty times the ordinary galvanic value. Fairbrother worked with an 80 mesh Jena "Gerate" glass powder and various aqueous solutions of electrolytes. The values for i_w/i_q given by his work, with solutions of potassium chloride and hydrochloric acid, are considerably smaller than those of Table VI; but the variety of glass employed was different from that of the present work, and it is possible that the conditions obtaining in electro-endosmotic experiments, where the liquid is allowed to flow freely through the diaphragm, may not have been reproduced with the diaphragm and solution confined in a conductivity cell.

The relation between the interfacial potential ζ and the charge σ per unit surface of each face of the electrical double layer‡ is given by the expression

$$\zeta=4\pi\sigma\delta/D \qquad (3)$$

where δ is the thickness of the electrical double layer and D the dielectric constant.

* Proc. Roy. Soc., 106, 315 (1924).

† *See* Stock, loc. cit., and Fairbrother, Jour. Chem. Soc., 125, 2495 (1924).

‡ *See* Freundlich, "Kapillarchemie," p. 329 (1922).

It follows, for a given value of σ, that ζ varies with the thickness of the double layer. There appears to be practically no experimental data in regard to the dependence of δ on the concentration of the solution, but the conclusions of Gouy* on theoretical grounds, as Freundlich† has pointed out, are opposed to the possibility that the rising branches of the ζ-concentration curves of Fig. 2 are to be attributed to increase in the thickness of the double layer. It appears from the graphs of Fig. 3 (and Table VI), however, that the thickness of the double layer increased initially with the concentration, attained a maximum value, and then regularly decreased with each of the three solutions studied; and, further, the curves of

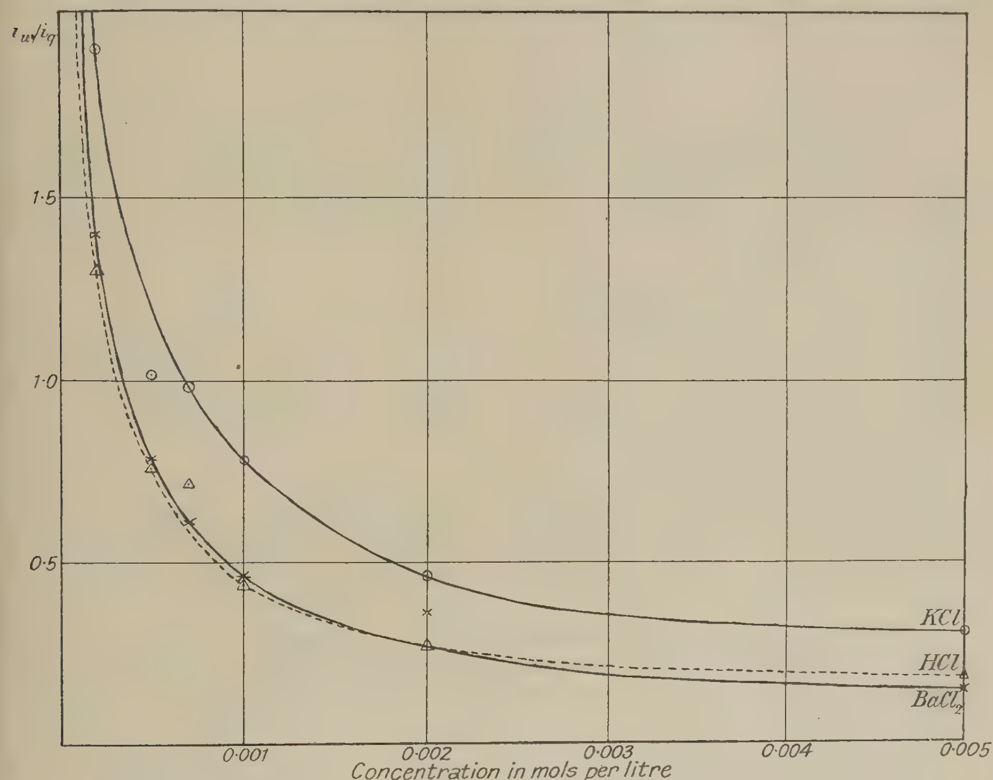

Fig. 5.—Dependence of the Conductivity on the Electro-Endosmotic Flow.

Figs. 2 and 3 are in the same relative positions with the exception of the rising branches for the solutions of hydrochloric acid. The maxima in the curves of Fig. 3, however, occur at somewhat lower concentrations than those in the curves of Fig. 2.

It follows from equation (3) that, within the range of concentration of the present work, σ, the charge per unit surface of each face of the electrical double layer, is proportional to ζ/δ, and therefore to ζ/t, where t is given by $\dfrac{\zeta^2}{\lambda i_w/i_q}$ (see p. 373). Values

* Loc. cit.
† "Kapillarchemie," p. 352 (1922).

of $\zeta/t \times 10^4$, calculated from the data in Tables IV and VI, are given in column 8 of Table VI. The result follows that the negative charge per unit surface of the wall layer in pure water actually increased with the concentration over the whole range of observations with solutions of barium chloride and hydrochloric acid; with solutions of potassium chloride the negative charge increased with the concentration from 0·0005 molar onwards.

In regard to the physical significance of the results for δ and σ, it is pointed out that these quantities are not directly connected with the actual distribution of charges in the neighbourhood of the wall, but relate to the Helmholtz electrical double layer which Gouy* has shown to be equivalent to such a distribution.

Summary of Results.

(1) The results indicate that the potential (ζ) of the interface glass-aqueous solution increases initially with the concentration, attains a maximum value, and then regularly decreases with solutions of hydrochloric acid, potassium chloride and barium chloride, in agreement with the general result of Kruyt in stream potential determinations.

(2) Higher values of ζ at concentration below 0·0007 molar were obtained when the solutions were prepared with laboratory distilled water (specific conductivity 8×10^{-6} recip. ohms), instead of with conductivity water (specific conductivity 10^{-6} recip. ohms), indicating, in the case of solutions of barium chloride, entire disappearance of the maximum in the ζ-concentration curve. This result indicates the importance of employing water of a high degree of purity in electro-endosmotic determinations.

(3) Measurements of the current flowing through the diaphragm during each determination of electro-endosmotic flow give results in harmony with the conclusions of Smoluchowski, from theoretical considerations, that electro-endosmosis must increase the ordinary galvanic conductivity in consequence of the surface current produced.

(4) The application of the formula derived by Smoluchowski to the data under (1) and (3) indicates that the thickness of the electrical double layer also reaches a maximum with increasing concentration in the case of each of the three solutions studied.

(5) The data for ζ and for the thickness of the electrical double layer lead to the result that the negative charge per unit surface of the wall layer against glass increases with the concentration up to 0·005 molar (the highest concentration of the present work) with solutions of hydrochloric acid and barium chloride; with solutions of potassium chloride the charge increases with the concentration from 0·0005 molar onwards.

So far as a search of the literature has been made, this Paper records one of the first systematic attempts to investigate experimentally the dependence of the thickness and the charge of the electrical double layer on the electrolyte concentration of the solution.

The author wishes to express his thanks to Professor Albert Griffiths for the interest he has taken in this investigation.

* Loc. cit.

DISCUSSION.

Mr. F. E. SMITH said that the Paper was of considerable interest, and the results appeared to have been obtained with great care. The author's glass powder diaphragm had worked satisfactorily, but personally, in using a similar diaphragm with $AgNO_3$ as the electrolyte, he had experienced the difficulty that with currents above a certain strength silver becomes deposited on the glass, and thereafter the greater part of the current passes through the metallic silver instead of through the liquid. This phenomenon of electrostenolysis had been very little investigated, and he recommended it to the author's attention.

Prof. A. GRIFFITHS said that the author had made some useful improvements in the experimental method, and on the theoretical side had shown the intimate relation between the P.D. across the double layer and the thickness of the latter. He had originally suggested that the author should take up this subject, because he had experienced certain difficulties in diffusion experiments which might possibly be accounted for by electro-endosmosis. In the diffusion apparatus employed water flowed very slowly through a long capillary tube into a wide chamber, and then again through a capillary tube. Whenever the water in the chamber was taken out and replaced the viscous resistance to the flow of the water was unaccountably increased for a time, and it seemed possible that potential differences of concentration of the solute in different regions of the tubes might set up electro-endosmotic effects which would account for the phenomenon. Prof. Griffiths had obtained a good deal of light on the question from the author, and hoped that the latter would extend the investigation.

Dr. H. BORNS asked why glass was selected for the diaphragm. For experiments of this kind the diaphragm should be chemically indifferent, but this could not be the case with glass. Powdered quartz or carborundum might be used, but even these substances might not be quite unexceptionable.

Mr. R. P. FUGE asked whether the cylinders on either side of the diaphragm were open to the atmosphere. Otherwise a difference of pressure might arise which would affect the results obtained.

Dr. D. OWEN asked which of the variables occurring in the author's fundamental equation were measured directly, and which represented hypothetical quantities.

AUTHOR'S reply: In reply to Dr. Borns, glass was selected for the diaphragm so as to obtain electro-endosmotic data for comparison with the results of Kruyt and others in stream-potential determinations with glass capillaries. In the view of Freundlich,* the slight solubility of the glass is an important factor in the formation of the electrical double layer.

In regard to Mr. Fuge's inquiry, the corks carrying the electrodes were provided with grooves, so that the cylinders on either side of the diaphragm were open to the atmosphere.

In reply to Dr. Owen, and as indicated in the Paper, all the variables occurring in the fundamental equation must be regarded as representing hypothetical quantities in so far as they are not directly connected with the distribution of charges in the neighbourhood of the diaphragm wall, but relate to the Helmholtz electrical double layer which Gouy has shown to be equivalent to such a distribution. The values given in the Paper as relating to the quantities mentioned are derived from direct measurements (*a*) of the liquid flow; (*b*) of the applied potential; and (*c*) of the current flowing through the diaphragm.

It is interesting to note, in connexion with the point raised by Dr. Owen, that Miss Laing and McBain† have recently proposed a migration theory of electro-kinetic phenomena in which an endeavour is made to avoid the use of hypothetical quantities. The work of Miss Laing with solutions of sodium oleate lends support to the views put forward, but further experimental verification would appear to be necessary before the theory can be regarded as definitely established.

* "Kapillarchemie," p. 347 (1922).

† Jour. Phys. Chem., 28, 673 (1924); Ibid., 28, 706 (1924).

XXXVII.—THE LATENT HEAT OF FUSION OF SOME METALS.

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ABSTRACT.

The latent heats of a number of the commoner metals have been measured by determining the total heat of liquid and solid from a series of initial high temperatures.

The calorimetry was by the method of mixtures, introducing several refinements, of which the chief were the use of fairly large charges of metal (of the order of 2 kilograms), and a device by which the hot charge was not allowed in contact with the water of the calorimeter until the latter was completely closed ; this eliminates error due to production and escape of steam, with a consequent loss of heat. The device referred to consisted in the provision of a sheet metal vessel suspended by threads from the main lid of the calorimeter. The aperture through which the charge was introduced was closed by a rotating lid, in the main lid, and the crucible being introduced, was submerged after the closing of this smaller lid by means of a wire passing through an eyelet in the base of the calorimeter, and out at the top.

The results for the latent heat are given below :—

Metal.	Melting point, °C.	Latent Heat. (Calories per gm.)
Aluminium	657	92·4
Antimony	630	24·3
Bismuth	269	13·0
Lead	327	$6{\cdot}2_6$
Magnesium	644	46·5
Tin...	232	14·6
Zinc	420	26·6

The Paper also contains values for the specific heats up to the melting point, obtained by differentiation of the temperature-total heat curves.

INTRODUCTION.

THE primary object of the investigation recorded in this Paper was the determination of the latent heat of fusion of the commoner metals. Although many workers have studied this problem in the past, the published data reveal astonishing discrepancies. Aluminium, for example, has had the values below ascribed to this physical constant.

Latent Heat of Aluminium.

Date.	Observer.	Latent Heat calories per gram.
1886	Pionchon	80
1904	Glaser	77
1911	Greenwood	93
1914	Lascento	64
1919	Wüst	94

In other cases, such as those of antimony and magnesium, we have been unable to find any recorded values. It was, therefore, decided to undertake experimental work, with a view to determining the latent heat of the following metals :—

Aluminium, Antimony, Bismuth, Lead, Magnesium, Tin and Zinc.

It has also been possible to determine the mean specific heats of these metals over a range of temperature.

Review of Previous Work.

Researches on the thermal capacity of metals at high temperatures have occupied the attention of many workers in the past 100 years, so it is desirable to give a sketch of their methods before describing new work.

Historically, one of the earliest workers was Rudberg,[1] who in 1830 determined the latent heat of lead, his value 5·86 comparing very well with the more recent determinations. He employed the method of cooling and, by comparing the rates of cooling of the metals whose thermal constants were unknown with that of mercury, which was assumed, he deduced the latent heats.

Person's[2] work dates back to 1848. He employed a calorimetric method and in the case of lead worked with specimens weighing 680 grams. The fusion points of the metals were determined by mercury thermometers, the glass of which was "cristal de Choisy-le-Roi." He corrected the readings of these thermometers to the scale of the gas thermometer by means of Regnault's table.

The Table below shows how his values of latent heats and of the fusion points compare with those obtained by us :—

Metal.	Latent Heat. Person.	Latent Heat. A. & G.	Melting Point (Person). Hg. therm.	Melting Point (Person). Air therm.	Melting Point (Present day values).
Tin	14·252	14·6	235·0°	232·7°	232
Bismuth ...	12·640	13·0	270·5°	266·8°	269
Lead ...	5·369	$6{\cdot}2_6$	334·0°	326·2°	327
Zinc ...	28·13	26·6	433·3°	415·3°	418

Spring[3] in 1886 investigated a series of tin lead alloys and in the course of these experiments determined the latent heats of fusion of tin and lead.

Pionchon,[4] a pupil of Berthelot, also carried out investigations about 1886 by the usual calorimetric method of mixtures.

Attention might be drawn to his method of measuring temperatures. He adopted Violle's method in which a small ingot of platinum was heated alongside the specimen and dropped into water. His temperature scale read about 50°C. low at 950°C.

Richards[5] (Chem. News, 68, 1893) criticizes Pionchon's value and states that the total heat of liquid aluminium at its melting point is 258·2, instead of the value 239·4, given by Pionchon.

Heycock and Neville[6] in 1897 found the latent heat of fusion of zinc by an indirect method. They made observations of the depression of the freezing point on adding a second metal and of the absolute temperature of the freezing point of the alloy. They then calculated the latent heat from the formula

$$\delta\theta = 0{\cdot}0198\ \theta^2/L$$

where $\delta\theta$ is the atomic depression of the freezing point and θ the absolute temperature of the freezing point. They found

$$\delta\theta = 5{\cdot}11$$

Hence L for Zinc=28·33 cals.

In 1903 Robertson,[7] at the conclusion of a Paper dealing with another subject, states that he has determined calorimetrically the latent heats of several metals. In the absence of detail it is impossible to assess the value of his results.

Harker and Greenwood[8] (1905) employed the calorimetric method with one notable modification. The metal sheathed in silica was dropped, not directly into

the calorimeter water, but into a funnel-shaped brass tube filled with calcined precipitated hydrate of magnesia, which formed a very light powder.

The object of the device was to prevent the splashing of the water which occurred if the metal was dropped in directly. The device had, however, the drawback that it retarded the attainment of temperature equilibrium between the metal and the water.

Guinchant[9] (1907), in a very brief Paper without illustrations, describes some experiments on the latent heat of silver nitrate by the usual calorimetric method, and mentions an electrical method by which he determined the latent heat of tin and obtained the value 14·3. He employed a silvered Dewar vessel surrounded by a thick layer of asbestos paper and by metallic reflecting shields. At the bottom of the vessel was placed an electric heater. The material to be studied occupied 30 c.cs. and was placed within the heater.

He determined the heat loss by a separate experiment in which the electrical energy required to maintain a series of steady temperatures was measured.

Mazzotto[10] in 1910 adopted the "cooling curve" method. He was investigating the lead tin alloys and in the course of the research determined the latent heats of these two metals.

In 1913 he published a further Paper[11] dealing with the tin cadmium series.

G. D. Roos[12] (1916) obtained the latent heats of magnesium and aluminium by a somewhat involved process. He made a comparison of the cooling curves of these metals with those of metals of known latent heat under identical conditions of experiment, reducing the observations by a method proposed by Tammann. The procedure followed was to plot the rate of cooling against the time. The latent heat is given by the equation $mR=C\Delta Zf(V)$,

where m is mass of metal,
R its latent heat,
C a constant,
ΔZ the duration of freeze,
$f(V)$ a function of the rate of cooling at the maximum, which corresponds to the rate of cooling just after the completion of the freeze.

The form of the function $f(V)$ was determined by utilizing the values quoted in Table below :—

Metal.	Latent Heat.	Observer.
Tin	14·25	Person
	14·65	Spring
	13·6	Mazzotto
	14·05	Robertson
Bismuth	12·4	Mazzotto
	12·64	Person
Cadmium	13·7	Person
Lead	5·32	Spring
	5·37	Person
	5·37	Mazzotto
	6·45	Robertson
Zinc	28·0	Mazzotto
	28·1	Robertson

It might be remarked here that the values in the above Tables were by no means representative of the data known at that time. For example, in the Table of values for tin the values given by Glaser[13] (1904), Wüst[14] (1919), Guinchant[9] (1907) have been ignored. Again, in the case of zinc the values of Heycock and Neville,[6] Lascento,[15] Greenwood,[8] and Glaser[13] were omitted. These range from 26·0 to 29·9.

Taking the latent heat of Cadmium as unknown, Roos calculated it from the value of each of the other four metals separately, assuming $f(V)$ to be of the form V^n and trying various values for n. The value of n which gave the best agreement for the latent heat values of Cadmium deduced from the various known latent heat values of the other metals was assumed to be the correct one.

Calculated Value of the Latent Heat of Cadmium.

Comparison Metal.	$n=2{\cdot}0$	$n=2{\cdot}1$	$n=2{\cdot}2$	$n=2{\cdot}3$
Zn	14·3	13·97	13·62	13·3
Pb	13·6	13·63	13·71	13·8
Bi	13·2	13·50	13·73	14·0
Sn	13·3	13·58	13·82	14·1

The most consistent values are obtained by taking $n=2{\cdot}2$.

The defect of this procedure is that the resulting value is subject to considerable uncertainty if the latent heat values of the comparison metals are not absolutely correct. He assumes the same value for n over a temperature range from 430°C. to 660°C. His value for aluminium is 80, whereas the value found in the present investigation was 92·4.

Roos checked this indirect method by a direct calorimetric determination of the total heat of specimens of liquid magnesium and liquid aluminium sealed in quartz tubes when cooling from 700°C. down to room temperature. To obtain the latent heat from this total heat, it was necessary to subtract the heat given up by the liquid in cooling through an interval of 50° and that given up by the solid in cooling from the freezing point down to the temperature of the calorimeter.

The total heat of the solid was deduced by extrapolating other observers' values for the specific heat and that of the liquid was deduced from that of the solid, together with the latent heat, by means of Tammann's rule

$$\frac{L}{T}=C_1-C_2$$

where L is the latent heat,
T is the absolute temperature of the melting point,
C_1 and C_2 the specific heats of the liquid and solid respectively. The agreement was remarkable.

Aluminium 80 by the cooling method
82 ,, ,, calorimetric method.
Magnesium 70 by the cooling method,
72 ,, ,, calorimetric method.

It is difficult to understand why he did not measure the total heat in the solid state up to the freezing point.

Wüst, Meuthen, and Durrer[14] (1918) employed an apparatus based on that of Oberhoffer. It was a combination of the ice calorimeter and vacuum furnace. For temperatures below 1,300°C. a nichrome-wound furnace was employed, while for higher temperatures a carbon spiral furnace was substituted. With this furnace a temperature of 1,600°C. could be reached in 3 minutes. This rapid raising of the temperature was necessary because with a slower rate of heating the walls of the glass enclosure became too hot.

The metal specimen was contained in a fused silica envelope, the ratio of the weight of the silica to that of the metal being from one-half to one-fifth, but as the specific heat of silica is about fivefold that of tin and lead, the correction for the heat capacity of the envelope became of serious magnitude in these experiments. The use of the ice calorimeter sets a limit to the size of specimen which can be manipulated conveniently. The use of small-sized specimens in calorimetry at high temperatures is not to be recommended, as the heat loss in the transference period becomes of serious magnitude. The experiments appear to have been carried out with care and thoroughness, but their values differ markedly from those of other observers.

White[16] has made the following criticisms of Wüst's methods :—

"His furnace was in a highly exhausted tube, which extended down into an ice calorimeter. The solid metals were ordinarily used bare, but were enclosed in silica glass when they were to be melted. Comparisons with the three solid metals, silver, gold, copper, up to 900° or 1,000° showed no difference, due to enclosure, in the specific heat so observed. The furnace thermel—i.e., thermo-electric thermometer—which was, as in our work, alongside the specimen, was found to be at the same temperature. In these special tests, as in most of the regular observations, the agreement was usually to 1 per cent. The tests and agreements reported are thus entirely favourable.

"The furnace, however, was entirely open at the bottom, which presumably caused much greater temperature difference through radiation than there were in our carefully-partitioned furnace. The high vacuum should have greatly diminished conduction and convection of heat, leaving heat transfer dependent on radiation. This evidently has a tendency to make the temperatures of enclosed bodies depend more on that of distant objects and on possibly variable radiating power. In Wüst's calorimeter the specimen fell into a metal box with a sheet nickel lid, which, still surrounded by vacuum, rested in a glass tube. The heat transfer was thus probably almost entirely by solid contact and radiation, and would, therefore, tend to vary with slight changes in the lie of the specimens or in the character of their surfaces, causing variations in the amount of heat escaping upward. In our case the specimen was dropped at once under water, and most of the heat transfer was over in the first minute. Wüst's agreement with the work of others is not very good. For the six metals, aluminium, chromium, cobalt, copper, nickel and silver, he differs in every case by from 4 per cent. to 8 per cent. at 100 deg. from Tilden or Schübel, who usually agree with each other to 1 per cent. At 500 deg. Wüst's discrepancy is less, but compared with specially accurate determinations in the Geophysical Laboratory, his value for silica glass, though high at 100 deg., is 5 per cent. too low at 900 deg. He agrees to 2 per cent. or better with our value for platinum from 200 to 1,400 deg."

Iro Iitaka[17] (1919) has carried out an investigation into the variation of the specific heat up to the melting point and the heat of fusion of some metals. He employed the method of mixtures with water or aniline as calorimetric liquid, the latter liquid being used to avoid explosion when the metal introduced was molten. The specimen was always fitted in a quartz vessel, and by making blank experiments with the empty container the loss of heat in the transit from the furnace to the calorimeter was allowed for. The water equivalent of the calorimeter was determined by dropping pure lead heated to 250° C. into the calorimeter. Four experiments gave the values 14, 14, 15, 15 (mean 14·5). Calculation of the water equivalent from the weight of copper, glass, etc., gave the value 13. It is stated that the temperature of the specimen was assumed to be uniform and in equilibrium with the thermoelement if the latter remained constant for about 10 minutes.

The results finally quoted by Iitaka take into account the values given by previous workers : the effect of this procedure has been generally to raise the values above the values actually found in his own experiments.

Walter P. White[16] (1921) has described experiments on the latent heats of fusion of two metals, nickel and monel metal, which have not been studied in the investigation described in this Paper. Specimens weighing about 27 grams were contained in closed silica glass tubes. The weight of metal was about 27 grams and the weight of the silica sheath 8·5 grams. The work was carried out with all the refinements of technique of this experienced investigator, and the only point of criticism is the small weight of material experimented with.

The results were checked by pouring directly into the calorimeter, nickel just ready to solidify, and agreement to about 2 per cent. with the furnace method was obtained.

In the present investigation the " method of mixtures " was employed, as this offered the simplest solution of the main problem, namely, the determination of the latent heats. It might be mentioned in passing that an electrical method was also tried. In this the metal was maintained in the solid state at an initial temperature which was very little below its melting point, and then the amount of electrical energy required to raise it to a temperature slightly above the melting point was determined by measuring the watts dissipated in a heating coil immersed in the metal.

The results obtained by the electrical method for the one metal tried—lead—were in good agreement with those obtained by the " method of mixtures." The " method of mixtures " has inherent limitations when it is desired to measure the variation of the specific heats of metals with temperature, and it is probable that the electrical method will ultimately be developed for this.

Two practical difficulties are encountered when applying the " method of mixtures " to high-temperature measurements :—

(1) Heat loss in the transfer of the metal from the furnace to the calorimeter.

(2) The formation of steam when the hot metal strikes the water.

As regards the first, various expedients have been tried to minimise the error due to the cooling during the transfer.

For example, the furnace may be mounted directly over the calorimeter and

the crucible dropped right through into the water in the calorimeter. The difficulty which then arises is elimination of the heat transfer from the furnace to the calorimeter, especially when it is opened directly over the calorimeter.

In the present series of experiments the error due to heat loss in transfer was largely diminished by a different procedure. A considerable quantity of metal was used (of the order of a hundredfold that employed by previous investigators), and the furnace was mounted alongside the calorimeter jacket but well shielded from it. The advantage of this procedure is obvious, doubling the dimensions of the specimen increases the heat capacity eightfold, whilst the heat loss in transfer, being proportional to the area, is only multiplied fourfold.

Similarly, the actual calorimetry is simplified, since a large weight of water may be used without the temperature rise becoming too small to be measured accurately. Consequently, in all these experiments samples ranging in weight from 4 lb. for aluminium to 7 lb. for lead were used.

The second practical objection to the method of mixtures was overcome by the use of a simple device for completely enclosing the hot charge in the calorimeter before the water had access to it. Consequently when it actually came into contact with the water the steam formed could not escape from the calorimeter.

We may now consider the experimental arrangements in detail.

The Furnace was an electrical resistance furnace sufficiently deep to provide a length of about 8 ins. over which the temperature was fairly uniform.

The Crucible, of iron or graphite, was supported in the uniform-temperature region of the furnace in such a manner that it could be transferred rapidly to the calorimeter.

The temperature of the test specimen was measured by a thermoelement enclosed in a sheath and well immersed in the molten metal or in a hole drilled in the solid metal.

A crucible was always used, whether the metal was in the solid or liquid condition, for the reason stated in the discussion of the " heat loss in transfer."

When working with metals which did not attack iron, crucibles of this material were used, as they had the advantage of low thermal capacity. For the other metals graphite crucibles were adopted, as this material was found to be well suited to working with oxidisable metals.

The thermal capacity of the crucibles was determined by making " blank " experiments in which the empty crucible was heated up and transferred in a similar manner to that followed in the main experiment.

The Thermocouple for Measuring the Temperature of the Heated Metal.—A platinum, platinum rhodium thermoelement was used. Before the experiment it was calibrated by intercomparison with standards whose temperature-E.M.F. curves had been determined by the following fixed points :—

Sulphur	Boiling point.	444·5°C.
Antimony	Freeze point.	630°C.
Sodium Chloride	,,	801°C.
Gold	,,	1,063°C.
Copper	,,	1,083°C.

After the completion of the series of experiments the calibration of the thermo-element was checked at the freezing point of salt (Na Cl), and the boiling points of water and sulphur. The original calibration was confirmed by these checks.

The temperature of the metal in the furnace was read to an order of accuracy

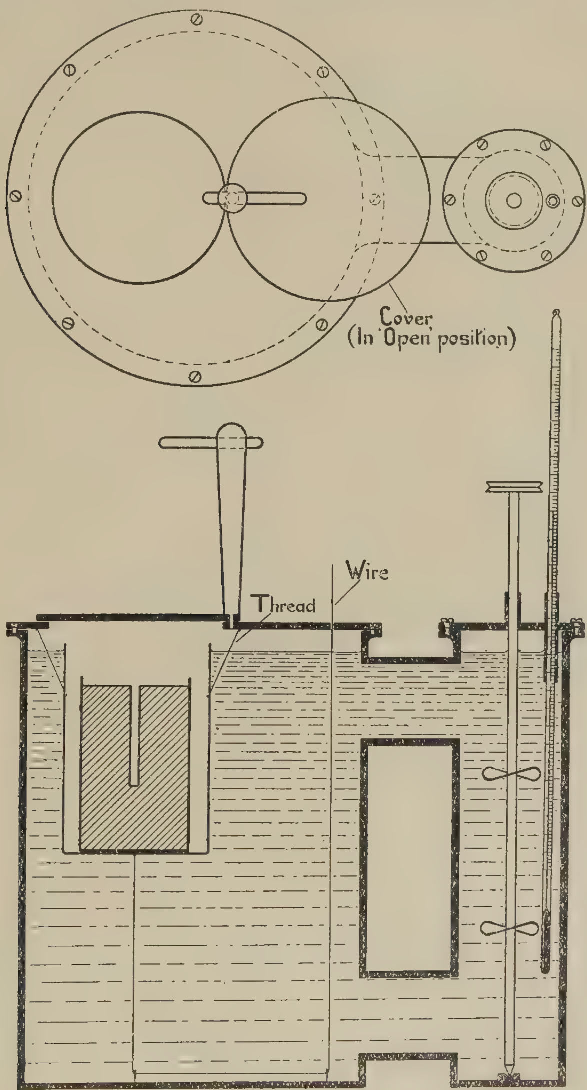

FIG. 1.

of 0·5°C. An uncertainty of 0·5°C. in the temperature of the molten metal would not cause an error of more than $\frac{1}{4}$ per cent. in the latent heat determination in the most unfavourable case of the metal with the lowest melting point, bismuth.

The Calorimeter.—This was of the form shown in Fig. 1, which shows a section (with the lid closed) and a plan (lid open). The main vessel was 12 in. in diameter by 19 in. in depth. The dimensions were so proportioned that the average temperature rise of the water on dropping in the heated metal would be about 5°C. or 6°C.

Thorough mixing of the water in such a vessel is important, and the method adopted by us will be seen in Fig. 1. Alongside the main calorimeter is a smaller vessel, 4 in. in diameter, connected to it by two wide pipes. The stirrer consists of two propellers on a shaft running the length of this chamber, and rotated by an electric motor. The blades of the propeller are so inclined that the water in the smaller chamber is lifted and thrown through the upper pipe into the large chamber. The thermometer is inserted through the tube seen projecting through the top of the small chamber.

The main vessel of the calorimeter was closed by a heavy cover with a 5 in. hole bored in it. This hole could be closed quickly by a well-fitting rotating lid, the secondary lid being manipulated by a wooden handle projecting up out of the enclosure. Reference has already been made to the desirability of preventing the escape of steam when the hot metal is plunged into the calorimeter. The device employed to overcome this was very simple and effective. A sheet metal vessel was suspended by three threads from the top of the calorimeter with the open mouth just above the surface of the water. The crucible was placed in this vessel in the first place, and the second lid of the calorimeter closed quickly. The vessel was then drawn down under the water surface by means of a wire attached to its base, and passing through eyelets in the bottom of the calorimeter.

With this arrangement any steam formed could not escape, as the calorimeter was completely closed before the water came into contact with the hot metal. It was, of course, essential that both calorimeter lids should make good thermal contact with the body of the calorimeter. A film of Russian tallow was found to answer quite satisfactorily, as the rubbing surfaces had been machined true.

The calorimeter was constructed entirely of copper, with a small amount of solder for the joints. The water equivalent of the calorimeter was calculated from the weight of copper and the specific heat, and was about 1,820 gram calories. The quantity of water worked with was about 28 litres, hence an error of 1 per cent. in the assumed value of the specific heat of copper would imply an error of 0·06 per cent. in the latent heat values.

The Calorimetric Thermometers.—For the various ranges of temperature covered in the investigation, two thermometers were employed. One divided directly into hundredths of a degree between 13 and 20°C., and the other, used only in experiments with large temperature rises, divided into tenths. With the former thermometer readings could be taken to 1/500 of a degree, and with the latter to 1/100 of a degree.

To avoid parallax error, a lens was used for reading the thermometers. All the readings were corrected to the hydrogen gas scale.

Heat Loss in Transfer of Charge to Calorimeter.—In the experiments with the "method of mixtures," the heat loss in the transfer of the metal from the furnace to the calorimeter constitutes a possible source of error which demands careful scrutiny.

On consideration it will be seen that the relative magnitude of this heat loss diminishes with increase in the size of the specimen transferred, and in this investigation the samples varied from 1 to 5 kilograms in weight. In addition, the metal, whether solid or liquid, was always inserted into a crucible, and a "blank" test carried out with the empty crucible. It is reasonable to suppose that approximately the same heat loss would occur when the empty crucible was transferred as when it contained metal, for the actual magnitude of the temperature drop in any case is small and determined solely by the cooling area. The absolute magnitude of this heat loss is difficult to determine accurately, but an estimate of its upper limit was formed by making an experiment with an empty crucible to the surface of which a thermoelement was attached. This crucible was allowed to attain a steady temperature of 500°C., and, with the couple in position, it was transferred from the furnace as far as the calorimeter. The temperature change was observed by the movement of the spot of light of the galvanometer in the circuit of the thermoelectric potentiometer.

The cooling effect in the process of transfer amounted to 2·2°C. As the thermal capacity of the crucible was only about 1/10 of that of the average specimen plus crucible, the cooling of the specimen and crucible would be estimated as 0·2°C. The actual error in the final result is much less than this owing to the compensation provided by using the same procedure for the empty and filled crucible, and we may estimate that it is less than one part in a thousand in the latent heat.

Other Possible Sources of Error.—Besides the sources of error incidental to calorimetric measurements at ordinary temperatures, there was the possibility of heat loss consequent on the use of the inner vessel mentioned above. To avoid the formation of steam when the hot metal strikes the water, the crucible was first transferred into a vessel suspended below the opening of the calorimeter, the opening of the calorimeter being closed promptly after the insertion of the charge, and the vessel was then submerged some time later, so the possible heat loss from the lid needs consideration.

In the first place, it should be noted that the vessel was deep enough for the greater portion of the radiation from the crucible to be absorbed by the water surrounding the vessel. Of the heat which is radiated directly to the lid, most is absorbed by the thick copper and conducted to the water, but a small fraction of it is radiated from the exposed surface of the lid to the surroundings. This "radiation loss" from the lid was studied in some preliminary experiments in which the actual temperatures of the lid, the top and the sides of the calorimeter were observed by the aid of thermoelements pegged into the metal at various points. Hot metal was poured directly into the container and the temperatures of the calorimeter surface at various points observed for a considerable interval of time afterwards.

The maximum difference of temperature between the lid and the body of the calorimeter occurred after the lapse of 5½ minutes from the instant of pouring in the metal, by which time the metal had solidified and cooled very considerably. Now the average heat loss during this interval can be computed as that from a plate which is at an excess temperature of 0·7°C. above its surroundings during a time interval of 5½ minutes. This radiation from the plate was calculated to be 1·3 calories while the convection would be about six times this amount, or 7·8 calories.

Hence the total heat loss from the lid would amount to some 9 calories. This quantity may be compared with a minimum of 30,000 calories conveyed to the calorimeter by the hot metal.

That the use of the inner vessel leads to no errors of measurable amount has also been proved in two other ways. In the one a crucible of molten metal was allowed to remain in it for 22 minutes before submerging in the water. The total heat calculated from this experiment was found to be 3 per cent. low as compared with the values obtained in normal experiments. If the magnitude of the error is assumed to be roughly proportional to the time, then, had the normal procedure been followed, the container would have been submerged within 3 or 4 minutes, and the error would, therefore, be of the order of 0·2 per cent. It must be remembered, however, that the error caused by the "radiation" loss from the lid during the initial stage is even smaller than this, as the excess temperature is not produced immediately.

It might be noted in passing that experiments have been carried out similar in all respects except that in the one case the container has been used, while in the other, it has been dispensed with and the charge dropped into the water. There is, of course, always the possibility of steam formation in the latter case, but the quantity formed is variable. Usually the difference in the results obtained did not exceed ½ per cent.

The remaining sources of error in the calorimetric measurements may be discussed very briefly. The smallest temperature rise was 0·8°C., and was measured to 0·001°C. There was no correction for cooling of the calorimeter during the experiment. The largest rises were about 12°C., and the corrections were applied for heat loss from the calorimeter by the usual method, measuring the rate of fall of temperature after the maximum rise was attained. The temperature rises were corrected for calibration errors of the thermometers, and for the emergent stem error.

The mass of water used was weighed each time in the earlier experiments. Later, a measuring vessel holding about 10,000 cubic cm. was used as a measure, the weight to fill it to a definite mark on the narrow neck being found by weighing. The water equivalent of the calorimeter with its fittings was estimated by weighing it, and calculating from the specific heat. The same procedure was used for obtaining the water equivalent of the inner vessel and of the thermometer. The water equivalent of the calorimeter is probably known to the same order of accuracy as the quantity of water used in the calorimeter.

Results.—Each experiment gives the total heat over a temperature range from that of the furnace down to that of the calorimeter. Now the temperature of the calorimeter varies, being dependent on the temperature rise obtained, so to refer to a common datum temperature it has been necessary to apply a small correction to the results to reduce them to total heats from a specified temperature. This correction was calculated from the known approximate value of the mean specific heat at room temperatures. The total heat values were then plotted against temperature, and a smooth curve drawn through the experimental points. These curves are shown in Figs. 2 and 3 for the metals studied. It will be noted that in the cases of antimony and aluminium, there are experimental points below the observed freeze point, which clearly fall on the curve for the liquid state. Evidently these are

due to under cooling of the liquid. The actual freezing point was determined for each metal used by taking a cooling curve with the same thermocouple. Then

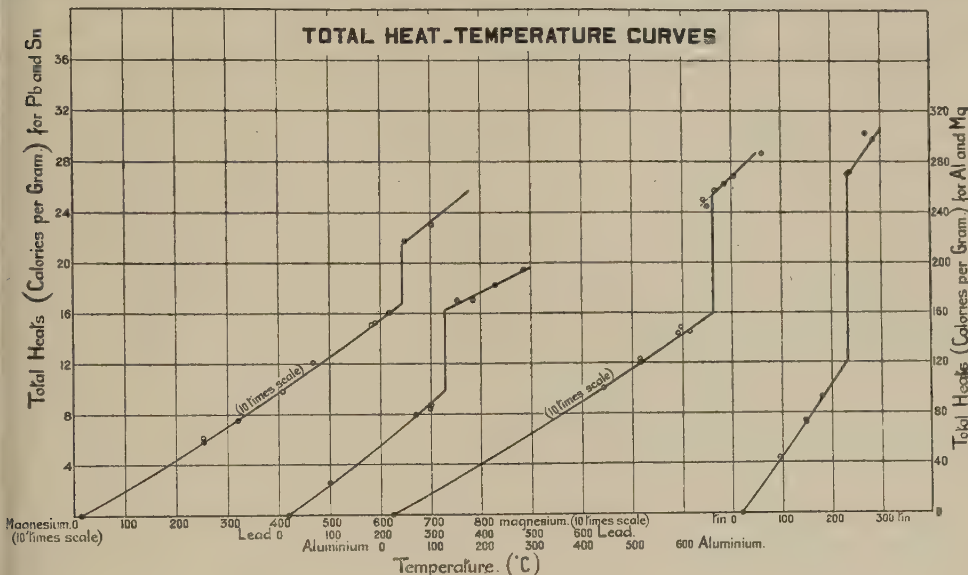

FIG. 2.

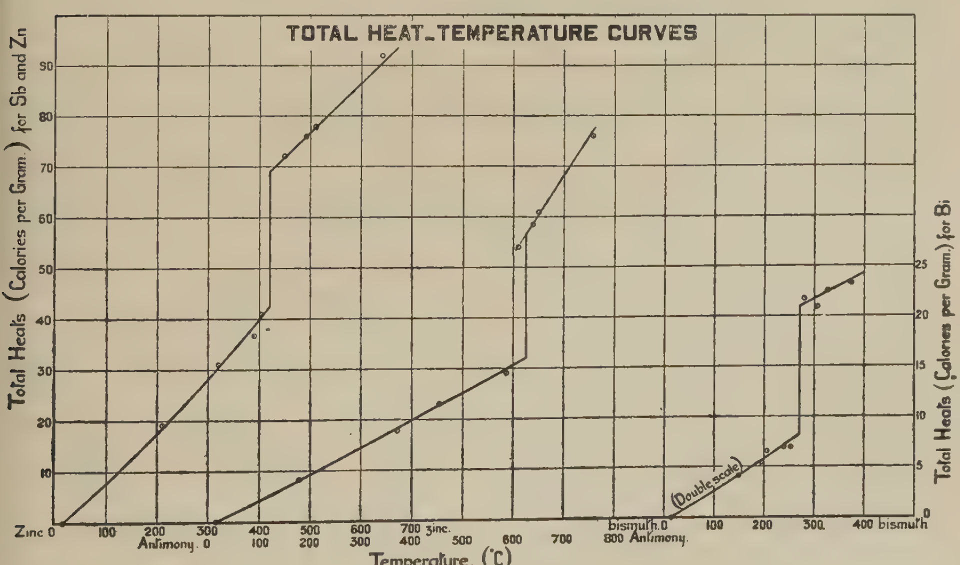

FIG. 3.

the latent heat is the difference between the total heats of solid and liquid, the specific heat being given by the slope of the curve.

A typical experiment on aluminium will serve as an example for all the metals :—

Initial temperature of water in calorimeter	19·08°C.
Final temperature (corrected for radiation losses)	23·80 „
Rise	4·72°C.
Correction for emergent stem	0·01 „
Calibration correction	−0·08 „
Corrected rise	4·65°C
Heat capacity of water (from its mass)	28,858 gms.
Heat capacity of calorimeter	1,821 „
Heat capacity of accessories	28 „
Total heat capacity	30,707 gms.
∴ Heat given up by metal and crucible	142,800 calories
Heat given up by crucible (from separate series of experiments)	28,255 „
Heat given up by metal	114,545 calories

Weight of metal = 782 gms.

∴ Heat given up per gm. of aluminium in cooling from 615°C. to 24°C. ... ... = 146·5 calories

Approximate specific heat of aluminium ... ... = 0·22 „

∴ Heat from 24°C. to 20°C. = 0·9.

Corrected total heat (to 20°C.) ... ... = 147·4 „

The remainder of the results for aluminium are given in Table below and Fig. 2.

Aluminium.—The material employed was the purest supplied commercially, the chief impurities being iron (0·13 per cent.) and silicon (0·15 per cent.). The melting point was found to be 656·5°C.

Heat given up by Aluminium in Cooling from θ to 20°C.

θ	Total Heat.	θ	Total Heat.	θ	Total Heat.
20	0·0	591	143·9	650	244·7
443	100·1	597	147·9	664	257·4
516	120·2	615	147·4	686	262·0
516	122·1	640	250·0	706	268·6
				763	286·7

Total heat at melting point—Liquid	252·6
Solid	160·2
Latent Heat	92·4 calories per gm.

Mean specific heat liquid from 657 to 760°C. = 0·66.

Specific Heat, Solid Aluminium, Deduced from Curve in Fig. 2.

Temperature Range.	Mean Specific Heat.
50° to 150°	$0{\cdot}22_6$
150° to 250°	$0{\cdot}23_4$
250° to 350°	$0{\cdot}24_5$
350° to 450°	$0{\cdot}25_7$
450° to 550°	$0{\cdot}26_8$
550° to 650°	$0{\cdot}28_7$

Comparison with Other Observers.

The total heat has been given by Lascento,[15] Tilden,[18] Schmitz,[19] Voigt,[20] Schubel,[21] Glaser,[13] Magnus,[22] Behn,[23] and Schimff.[24] A study of the observations shows that the low value for the latent heat obtained by Lascento is due to the abnormally high values obtained by him for the total heat of the solid metal. This may have been due to impurities, which would cause the melting point to spread out over a finite range of temperature, with a partial development of "latent heat" at temperatures below the true melting point.

The values given by the various observers for the latent heat are as follows :—

Pionchon	80
Lascento	64
Glaser	77
Wüst	94
Roos	82
	80

The last observer gives two results, one based on his determination of the cooling curve, and one in which he measured the total heat of the liquid. For the reduction of both results he relied on the values in the literature ; in the one case for the latent heats of comparison metals, and in the other for the total heat of the solid material. Wüst's value is extrapolated from a series of experiments on alloys of varying composition.

In addition to these total heats, the true specific heat has been measured, either over a small temperature range or by the electrical method, by the following observers :—

Jaeger and Diesselhorst[25]	18	0·2144
	100	0·2227
Griffiths and Griffiths[26]	−73	0·1899
	−23	0·2045
	27	0·2144
	67	0·2207
	107	0·2263
Nernst and Lindemann[27]	−38	0·1963
	58	0·2098
	160	0·2250
	283	0·2391

It should be stated again that we do not claim that the specific heats deduced by differentiating the total heat curve will compare in accuracy with direct "electrical method" determinations. Nevertheless, the agreement between our values and the others is as good as the agreement of the others among themselves.

Antimony.—This was kindly supplied to us by Mr. Cookson, of the firm of

Cookson & Co., through the good offices of Dr. Hutton, Director of the Non-ferrous Alloys Research Association. Its purity was stated to be 99·95 per cent., and the melting point as determined by us was 630°C.

The experimental results are given in the table below :—

Total Heat, Antimony.

Temperature.	Total Heat.	Temperature.	Total Heat.
17	0·00	609	54·11
176	8·30	638	58·59
372	18·06	650	61·00
453	23·14	755	75·98
592	29·06		

From the smooth curve :—

Total heat at melting point—Liquid	56·52
Solid	32·21
Latent Heat	24·3

Mean specific heat liquid from 630 to 760°C. $=0{\cdot}15_5$.

Specific Heat, Solid Antimony.

Temperature Range.	Mean Specific Heat.
150° to 250°	$0{\cdot}052_4$
250° to 350°	$0{\cdot}053_1$
350° to 450°	$0{\cdot}053_7$
450° to 550°	$0{\cdot}054_4$
550° to 620°	$0{\cdot}054_9$

Comparison with Other Observers.

Values for the total heat have been obtained by Schubel,(21) Behn,(23) Ewald,(28) Schimff(24) and Gaede.(29) The only observer we can trace who has given a value for the latent heat is Wüst,(14) his value being 38·9. No determinations of the specific heat appear to have been made, apart from those cited above as determinations of the total heat.

Bismuth.—The samples employed were also obtained for us through Dr. R. S. Hutton, from Messrs. Johnson, Matthey & Co., and the chief impurity was silver, to the extent of 0·013 per cent. We found that the freezing point was at 269°C.

The observations were as follows :—

Total Heat, Bismuth.

Temperature.	Total Heat.	Temperature.	Total Heat.
15	0·00	254	6·89
150	4·11	279	21·75
195	5·41	306	20·82
206	6·58	327	22·49
240	6·96	376	23·33

The values for the total heat of the liquid are rather unsatisfactory, possibly owing to some oxidation, and the accuracy of the latent heat will consequently be lower.

The results deduced are given below :—

Total heat at melting point—Liquid	... ...	21·3
Solid	... ...	8·3
Latent Heat	... ...	13·0

Mean specific heat liquid from 270 to 400°C.=0·019.

Specific Heat, Solid Bismuth.

Range.	Specific Heat.
50° to 150°	$0{\cdot}029_2$
150° to 250°	$0{\cdot}034_9$

Comparison with Other Observers.

Experiments on the total heats have been described by Voigt,[20] Schubel,[21] Stucker,[30] Ewald,[28] Magnus,[22] Person[2] and Schimff.[24]

The latent heats given by others are quoted below :—

Observer.	Latent Heat.
Person	12·6
Mazzotto	12·4
Iitaka	12·2
Wüst	10·2

The same remarks apply to the results of Wüst for bismuth as in the case of aluminium.

Lead.—The analysis of this showed the presence of 0·002 per cent. iron and 0·002 per cent. copper. It dissolved a little iron from the crucible, and after the experiments was found to contain 0·012 per cent. of iron. The oxygen was also determined afterwards and found to be 0·0046 per cent. by weight. The freezing point of the lead used was 326·5°C.

The following table gives the observations :—

Total Heat Load.

Temperature.	Total Heat.
18	0·00
100	2·52
269	7·94
288	8·41
300	8·72
354	17·04
385	17·05
429	18·29
486	19·42

Total heat at melting point—Liquid	... ...	16·18
Solid	... ...	9·92
Latent Heat	... ...	6·26

Mean specific heat liquid from 330 to 500°C.=$0{\cdot}020_5$.

Specific Heat, Solid Lead.

Temperature Range.	Specific Heat.
100° to 200°	$0{\cdot}031_1$
200° to 300°	$0{\cdot}034_0$

Other observers have given the following values for the latent heat :—

Mazzotto(10)	5·37
Spring(3)	5·32
Robertson(7)	6·45
Glaser(13)	4·78
Iitaka(17)	5·52
Wüst(14)	5·47
Person(2)	5·37
Roos(12)	6·37

Magnesium.—This metal oxidises extremely at temperatures just above its melting point. In addition, it reacts to a measurable extent with water at considerably lower temperatures. After a number of trials, it was found that the

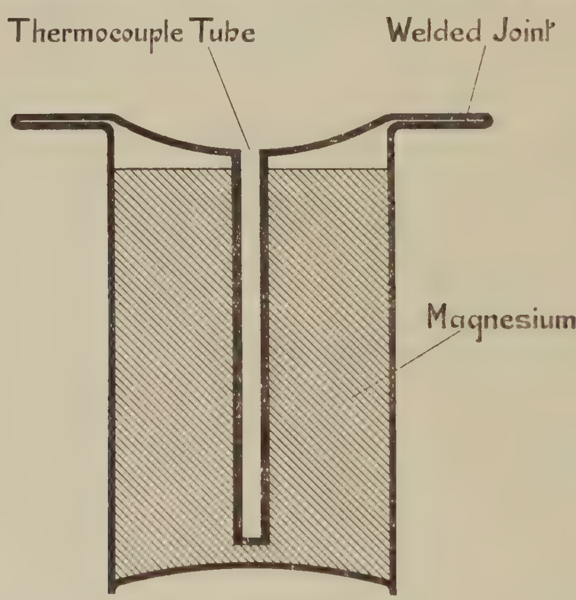

Fig. 4.

only way to prevent errors due to these causes was to enclose the sample completely in a metal container with all joints welded. The magnesium was cast into a block, turned down in a lathe to remove any oxide on the surface, and placed in the crucible (Fig. 4). The lid was then welded on. Thus no air beyond the amount initially present could enter, and the water of the calorimeter was also denied access to the magnesium. The shape of the crucible was intended to give it strength for resisting atmospheric pressure when only fluid was inside, without having to make it so

thick that its heat capacity would be a serious fraction of the total. The flange at the top serves to this end, and also removed the danger of setting fire to the magnesium when the lid was being welded on. It will be noted that the re-entrant tube for the thermocouple is attached to the lid in such a way that strains on solidification will not break it off.

One effect of completely sealing the sample inside a crucible was to increase the time taken for the calorimeter temperature to become steady on immersing the crucible. The final temperature was not attained, in fact, for about 10 or 15 minutes. Thus the heat loss from the calorimeter during the heat exchange required a somewhat larger correction than was the case in experiments with other metals ; for example, in one experiment the observed rise was 4·92°C., and the correction deduced from the rates of cooling before and after, was 0·053°C., a correction of fully 1 per cent.

The analysis of the sample of magnesium gave silicon 0·05 per cent., iron 0·02 per cent. The melting point being at 644°C.

The results are very concordant and are summarised below :—

Total Heat, Magnesium.

Temperature.	Total Heat.	Temperature.	Total Heat.
16	0·00	582	151·6
252	58·2	589	152·4
252	61·6	618	160·6
319	75·8	649	217·4
407	98·0	703	230·2
466	120·2	750	254·0

Total heat at melting point—Liquid	215·9
Solid	169·4
Latent Heat	46·5

Mean specific heat of liquid from 650 to 750°C.$=0{\cdot}26_6$.

Specific Heat, Solid Magnesium.

Temperature Range.	Specific Heat.
150° to 250°	$0{\cdot}025_8$
250° to 350°	$0{\cdot}026_4$
350° to 450°	$0{\cdot}028_0$
450° to 550°	$0{\cdot}029_6$
550° to 625°	$0{\cdot}030_0$

Roos found the latent heat to be 72.

Tin.—The tin employed melted at 232°C. and had the composition :—

Carbon	0·02 per cent.
Lead	Trace
Iron	Trace
Tin (by difference)	99·98

The individual determinations of the total heat gave the results below :—

Total Heat, Tin.

Temperature.	Total Heat.
18	0·00
93	4·45
148	7·22
148	7·37
180	9·25
233	27·01
237	27·19
270	30·24
287	29·76

Total heat at melting point—Liquid ... ... 26·90
Solid ... ... 12·27

Latent Heat ... ... 14·6

Mean specific heat liquid from 230 to 300 °C.=0·056.

Specific Heat, Solid Tin.

Temperature Range.	Specific Heat.
50° to 150°	$0{\cdot}056_9$
150° to 250°	$0{\cdot}058_1$

Comparison with Other Observers.

Iitaka and Pionchon have both quoted values for the specific heat of the liquid, and the latent heats given by a number of observers are collected in the table below.

Observer.	Latent Heat.
Rudberg	13·3
Person	14·3
Pionchon	14·6
Spring	14·65
Mazzotto	13·6
Robertson...	14·05
Glaser	13·6
Roos	14·2
Iitaka	13·4
Wüst	13·8
Guinchant...	14·3

Zinc.—This was a very pure electrolytic zinc, freezing at 420°C. The results were :—

Total Heat, Zinc.

Temperature.	Total Heat.
18	0·00
210	19·20
321	31·13
391	36·62
404	40·91
449	72·04
491	75·83
510	77·89
641	91·51

Total heat at melting point—Liquid	... ...	69·23
Solid	... ...	42·65
Latent Heat	... ...	26·6

Mean specific heat liquid from 420 to 500°C.=0·092.

Specific Heat, Solid Zinc.

Temperature Range.	Specific Heat.
100° to 200°	0·099
200° to 300°	0·105
300° to 400°	0·118

These increase more rapidly than usual with increase of temperature, indicating that the total heat curve should probably run somewhat higher at the intermediate temperatures. However, the difference in the total heats, to bring the specific heat curve down to a straight line is quite insensible in its effect on the total heat at any particular temperature.

Previous results for the latent heat have varied from 23 to 30, as shown in the table below :—

Observer.	Latent Heat.
Mazzotto	28·0
Person	28·1
Heycock and Neville	28·3
Lascento	27
Greenwood	26
Wüst	23
Glaser	29·9
Iitaka	23·1

The only value we have found for the specific heat of the liquid is that of Iitaka, 0·121.

Acknowledgments.

The investigation arose out of an inquiry of the Non-Ferrous Metals Research Association for information as to the thermal constants of the commoner metals. The authors desire to record their indebtedness to Dr. R. S. Hutton, Director of the Association, for his co-operation in securing suitable pure material ; to Dr. Kaye, Superintendent of the Physics Department, for the facilities for carrying out the work ; to Mr. A. R. Challoner, Observer, for his assistance in the construction of the apparatus and in helping with the observational work. We are also indebted to Miss V. M. Gayler, D.Sc., for several of the references.

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XXXVIII.—THE PIEZO-ELECTRIC QUARTZ RESONATOR AND ITS EQUIVALENT ELECTRICAL CIRCUIT.

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Abstract.

The quartz piezo-electric resonator is examined experimentally and theoretically with special regard to an equivalent electrical system which can represent it.

It is shown that, as theoretically predicted by Butterworth, such a resonator can be represented by an inductance, a resistance and a capacity all in series. These are pictured as in parallel with another small condenser and the whole is in series with a third condenser, the additional condensers representing air-gaps. The equations for the current in an oscillatory circuit, to which the resonator is attached, are developed and it is found that almost perfect agreement exists between the forms of current curve obtained theoretically and experimentally. This agreement is found to hold for longitudinal resonators of as low a frequency as 44,000 and for transverse resonators of as high a frequency as 15,000,000 periods per second.

It is next shown how the logarithmic decrement of the resonator may be obtained from a rectified line plotted from observation on the current in the oscillatory circuit as a function of frequency width across the crevasse which pierces the summit of the resonance curve.

The methods of analysis of the equivalent mesh into its components are next developed and it is shown that this analysis can be effected by carrying out a series of observations of the current at resonance when the air-gaps are varied by known amounts, or when the effective resistance of the oscillatory electrical circuit is given different known values.

The theoretical and experimental results are found to be consistent. The value of the shunting condenser is somewhat smaller than that measured at a neighbouring frequency outside the region of resonance. A possible explanation is offered.

The effects on frequency of response of variation of air-gap are studied and the difference between prediction and observation is discussed. This difference is only a few parts in a hundred thousand. In the case of transverse resonators remarkable effects occur when the air-gap is varied through the regions where its length is an integral member of half-wavelengths of the supersonic air waves produced by the vibration of the quartz.

The temperature coefficient of frequency of a considerable variety of resonators is examined over a range of temperatures up to 40°C. It is found that very diverse results are obtained and probable explanations are offered.

The effects of displacement of the resonator from the position of centrality are examined. These are shown to be small, but not quite negligible.

The current taken by the quartz mesh is then examined in some detail theoretically, and one or two experimental curves are given, together with a graphical method of deducing the curve of current from the constants of the quartz. A selection of theoretical curves for the conditions under which the experiments of Cady were made have been calculated. The curves are in all respects of the shape and form experimentally found by him.

A number of conclusions and suggestions terminate the Paper.

THE quartz piezo-electric resonator has been introduced by Cady who has published a number of valuable Papers(1) on their properties and form. G. W. Pierce(2) also has contributed valuable information on the subject showing the form, mounting and circuits of quartz oscillators whereby the resonant vibration is self-maintained by a valve in the same fashion that a tuning fork may be made self-maintaining. More recently he has published an account of some very accurate measurements of the velocity of sound at very high frequencies, using quartz oscillators as the source of sound.

Giebe(3) also has published a short Paper indicating a simple and elegant means

whereby the state of maximum resonant vibration may be rendered directly visible by mounting the resonator in a vacuum and observing the luminous glow between the surfaces of the quartz and the electrodes, consequent upon the large voltage gradient in the air gap at the regions where the alternating stress in the quartz is a maximum. In this manner the overtone modes of vibration may be rendered visible also. Other more or less popular accounts of the properties of quartz resonators and oscillators have from time to time appeared in the technical press.

The reader is specially referred also to the classical Paper by Sir W. Bragg[(4)] on the structure of α and β quartz.

Although, therefore, the form, construction and use of quartz resonators and oscillators may be considered fairly well known it is, perhaps, desirable to include in the present Paper the briefest description of the essentials of a piezo-electric quartz resonator.

Referring then to Fig. 1, we have a transverse section of a natural quartz crystal cut in a plane perpendicular to the optic axis. Any such section contains three electric axes (shown dotted), at angles of 120° to each other and parallel to the rectangular bounding faces of the crystal.

A bar or plate is cut from the section with its length perpendicular to one of the electric axes as shown at AB. The dimension of the piece in the direction

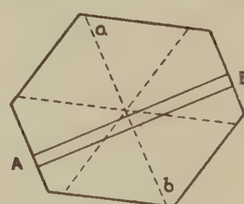

Fig. 1.—Cross-section of Quartz Crystal showing how a Bar or Plate is cut.

parallel to the optical axis of the crystal may be large or small. If it is small compared with the length AB we obtain a bar. If of the same order as AB we obtain a plate. If such a plate or bar is placed in an electric field applied in a direction perpendicular to its length, i.e., parallel to the electric axis, ab, the bar will experience two strains, one in the direction of its length and the other perpendicular thereto, i.e., along the direction of the applied field. These two strains are of opposite sign, so that, if for example, the bar becomes longer in the direction AB it becomes thinner in the direction ab. The two strains are such that the volume remains constant.

The strain across the bar has been called the longitudinal effect because it is along the direction of the applied field although transverse to the length of the bar.

It is clear that if an alternating electric field is applied to the bar it will be subjected to alternating stresses and strains both along its length and transversely thereto.

If the frequency of the applied field is adjusted to coincide with that of one of the free modes of vibration which can be maintained by such alternating stresses, a large resonant vibration will occur. The amplitude of this vibration and its rate of change with frequency will depend upon the mechanical damping of the quartz and upon its piezo-electric reaction on the applied field.

It is the very small damping coefficient and the permanence of form and constitution of natural quartz that render it specially valuable as a radio frequency standard when suitably cut and mounted.

It must be kept in mind in thinking of the various modes of vibration that a longitudinal vibration results from the transverse piezo-electric effect and vice versa.

Now a theorem has been enunciated by Butterworth(5) relating to a dynamical system in which mechanical vibrations may be produced by the reaction of an electric system upon it. It is shown that the mechanical vibrator may be replaced by an equivalent electrical oscillatory circuit coupled to the actual electric circuit in a manner depending upon the nature of the mechanical oscillator and the means whereby the transformation of electric into mechanical displacement occurs. The piezo-electric resonator is a mechanical vibrator falling within this class. For such a resonator the equivalent circuit given by Butterworth—with the addition of a small capacity K_2—is as shown in Fig. 2.

The system consists of an inductance N,* a resistance S and a capacity K all in series. These are shunted by another condenser K_1. Such a mesh represents

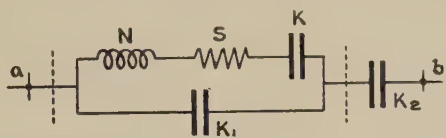

FIG. 2.—THE EQUIVALENT NETWORK REPRESENTING A RESONATOR MOUNTED BETWEEN ELECTRODES.

a piezo-electric resonator in which the electrodes are in contact with the surface of the quartz.

The constants N, K and S are related to the dynamical properties of the bar as follows—quoting from Butterworth :—

$$N=\alpha/B^2\,;\quad K=B^2/\gamma\,;\quad S=\beta^2/B^2$$

where α, β and γ are the constants of inertia damping, and restoration respectively in the fundamental equation of motion.

$$(\alpha D^2+\beta D+\gamma)y=Y$$

in which y is the displacement and Y is the displacing force. D is the operator d/dt. The displacing force Y is equal to B e, where e is the E.M.F. between the two surfaces of the quartz.

The constants α, β, γ are, therefore, simple physical constants of the quartz, whilst B is an electro-physical constant proportional to the piezo-electric effect. The value of B is measured by the mechanical stress produced per unit of electric field applied. It is analogous to the constant which would define the back E.M.F. produced in a wire vibrating in a magnetic field.

In the case of a bar or plate vibrating under its own internal stresses the

* Since writing this Paper a note has appeared in the Physical Review (Vol. 25, No. 6, Abs. 52, p. 895, 1925) which gives identically the same circuit for the quartz resonator, but the theorem referred to was published, and the experiments described here were in progress before this note appeared.

constants of inertia, restoring force and damping are, of course, distributed. For any given mode of vibration there will, however, be equivalent concentrated inertia, damping and restoring forces which may be considered constant for that mode.

If the resonator vibrates in an overtone mode such as that representing 3, 4, 5, 6, etc., segments, there will be a corresponding set of equivalent constants N, S and K, which will apply only to that mode.

It is not proposed in the present Paper, to examine closely the mathematical nature of the general equations given above in relation to the possible modes of vibration of the system, but to examine rather both algebraically and experimentally some of the properties of the equivalent electrical system of Fig. 2, and of other circuits upon which the resonance of a quartz resonator may be observed.

The resonator as usually mounted consists of a plate or bar of quartz in which the electrodes are separated from the surfaces of the bar by a small air gap. In this case we may represent the air gap by a small condenser K_2 in series, as shown in Fig. 2.

A very satisfactory method of using a resonator as a standard is that given

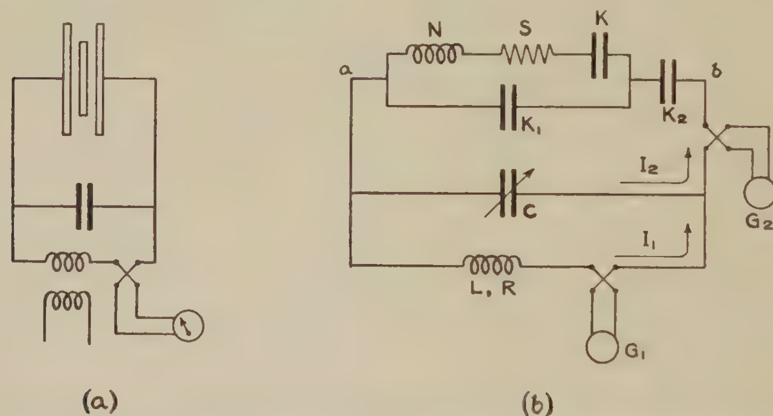

Fig. 3.—Mode of observing Resonance on a Resonator and the equivalent Electrical System.

by Cady in which the resonator with its electrodes is connected in parallel with the condenser of an oscillatory circuit tuned approximately to the resonance frequency of the quartz. A current-measuring device in series with the inductance coil of the oscillatory circuit indicates the sudden change in current occurring at the response frequency of the quartz.

This arrangement is shown diagrammatically in Fig. 3(*a*) and the complete electrical equivalent system is as shown in Fig. 3(*b*).

In this figure the piece of quartz itself is represented by N, K and S shunted by K_1. The two air gaps are represented by K_2.

A series of careful experiments is able to determine the validity or otherwise of the equivalent electrical network and will give valuable information regarding the actual values of the equivalent constants N, S and K and show how these depend upon the properties of the quartz, etc.

It is to be anticipated also that much may be learned regarding the constancy

of these quantities with respect to the physical condition of the specimen and its surroundings.

The experiments described herein have shown that a striking agreement may be obtained between the observed current I_1 (Fig. 3*b*) in the oscillatory circuit as a function of the frequency of the source and the calculated current in terms of the determined constants N, S, K and K_1. Equally good agreement is also obtained between theory and experiment with respect to the current I_2 (Fig. 3*b*) in the shunt circuit containing the resonator.

Before giving the experimental results and the comparison with those calculated it will be found helpful, in the formation of a clear mental image of the behaviour of the resonator, to consider the properties of the equivalent electrical mesh representing the resonator itself as an entity apart from the attached electrical circuit. We will then proceed to an examination of the properties of the complete system and will show how the analysis of the constants N, S, K and K_1 may be obtained from the experimental observations.

Referring to the mesh N, S, K, K_1 of Fig 3(*b*) we can find an equivalent virtual single series circuit consisting of an effective pure resistance S_0 in series with an effective pure capacity K_0 to replace the mesh. The values of S_0 and K_0 will, of course, be greatly dependent upon frequency. The equivalents S_0 and K_0 will be in series with K_2 and it is this simple series circuit which is in parallel with the oscillatory circuit.

It is convenient to use a resonant frequency, $\omega_0/2\pi$ defined by $NK\omega_0^2=1$ and to write q for $1-NK\omega^2$, where q is a small quantity proportional to a small change in frequency from that given by $\omega_0/2\pi$.

This expression constantly occurs in what follows. The frequency $\omega_0/2\pi$ will be spoken of as the true resonant frequency, although such a definition is open to some criticism. Another quantity of great importance is the term $SK\omega$, a quantity equivalent to the power factor of the condenser K.

$SK\omega\times\pi$ is equal to the logarithmic decrement per complete period of the resonator, and will be designated δ_2. To avoid the constant repetition of π in the formulæ $SK\omega$ will be written as φ_2, so that $\delta_2=\varphi_2\pi$.

Using this nomenclature it will be found that the quantities S_0 and K_0 are given by the expressions :—

$$S_0=\frac{SK^2}{K_1^2[\varphi_2^2+(q+K/K_1)^2]} \quad \ldots\ldots\ldots \quad (a)$$

and

$$\frac{1}{K_0\omega}=\frac{\varphi_2^2+q(q+K/K_1)}{K_1\omega[\varphi_2^2+(q+K/K_1)^2]} \quad \ldots\ldots\ldots \quad (b)$$

The magnitude which these quantities can assume is dependent mainly upon φ_2. This is a very small quantity—of the order 30×10^{-6} in a good specimen of quartz.

It is a property of a resonant electrical circuit that if for various chosen values of q as defined above we plot corresponding values of S_0 and $1/K_0\omega$ as ordinate and abscissa respectively, we shall obtain an almost perfect circle. From equation (*b*) it will be seen also that K_0 can assume negative values for values of q lying between 0 and $-K/K_1$. This is a very important property of the quartz, and is responsible for its behaviour when placed in an air gap between two electrodes. Since it so

happens that K/K_1 is a quantity of the order 1/100, the region of frequency through which $1/K_0\omega$ can be negative is small.

We have seen that the air gaps are considered as equivalent to a small series condenser K_2. If for any particular air gap represented by K_2 we choose such a value of q that $K_0 = -K_2$ the whole system between the points *ab* of Fig. 2 becomes equivalent to a non-inductive resistance S_1. It is clear that the maximum damping is produced upon the oscillatory circuit almost at this frequency. It is necessary to give the frequency at which this effect occurs a different name from the resonant frequency $\omega_0/2\pi$ as previously defined. It can be called the response frequency of the quartz. It differs theoretically from ω_0 by the quantity $-\frac{\omega_0 q_1}{2\pi}$, where q_1 is that value of q at which $K_0 = -K_2$. This condition is shown vectorially in Fig. 4. The curve AB shows a small part of the vector impedance circle diagram resulting from plotting $1/K_0\omega$ as abscissa against S_0 as ordinate for various values of q. Suppose the air gap is such that $1/K_2\omega$ is given by OQ, then, at a certain negative value of q represented by the point P on the curve, the value of $1/K_0\omega$ represented by ON will

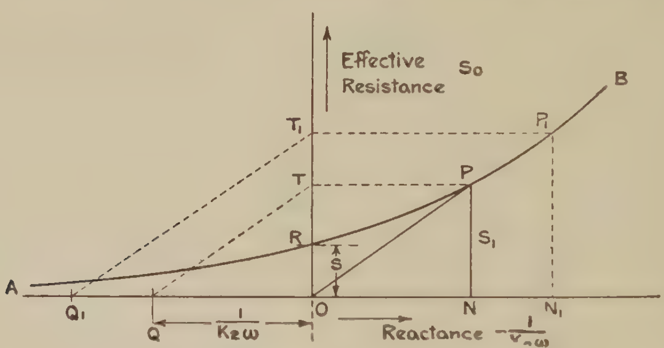

FIG. 4.—IMPEDANCE DIAGRAM OF A RESONATOR.

be equal and opposite to OQ. The resultant vector impedance across "*ab*" of Fig. 3(*b*) is therefore OT. With a larger air gap and hence a smaller value of K_2, the negative reactance $K/K_2\omega$ shown as OQ_1 will be greater. The response frequency will then occur at such a value of q as is represented on the curve AB by the point P_1. This is the larger negative value of q requisite to make ON_1 equal to OQ_1.

The effective resistance of the whole resonator has now the greater value OT_1, which will, therefore, not cause such a large reduction in the current in the oscillatory circuit LRC.

From these considerations it will be seen that the frequency of response is not quite equal to that which has been defined as the true resonant frequency of the quartz itself, but is a function of the air gap. When K_2 is infinite (no air gap) the response frequency is at the true resonant frequency, where $q=0$ and the vector impedance becomes S as shown by OR in Fig. 4.

It is perhaps desirable at this stage to anticipate the experimental results somewhat by giving the actual effective values of K, S, N and K_1 experimentally measured in a typical resonator.

For a bar about 7 cm. long, 0·15 cm. thick and 0·6 cm. wide, the following values have been found :—

$$K=0{\cdot}08\ \mu\mu\ \mathrm{F}.$$
$$S=1{,}500\ \text{ohms}.$$
$$N=160\ \text{henries}.$$
$$K_1=8\ \mu\mu\ \mathrm{F}.$$
$$\omega_0=275{,}000.$$

It will be seen that the reactance of K and N are very large indeed.

$\varphi_2=SK\omega$ is of the order 30×10^{-6}, giving the extremely small value of 1×10^{-4} for δ_2 the log. dec. of the resonator.

The diameter of the motional impedance circle of Fig. 4 is no less than 100 megohms. In order to show the resistance vectors OR, OT, etc., it has been necessary to magnify the ordinates by about 50, so that the circle really becomes an ellipse with a vertical axis. Since OR represents 1,500 ohms the major axis of the ellipse is about 300 metres long if OR is 5 mm. in the diagram.

We will now return to a consideration of the resonance curve of current in the inductance coil L of the oscillatory circuit LRC across which the resonator is shunted. It is this current which can easily be observed as a function of frequency, and of those other quantities in Fig. 3(b) which can be varied. By deductions made from the observations we can arrive at a complete analysis of the constants K, S, N and K_1.

The case under investigation is as shown in Fig. 5.

The resonator is the mesh $NSKK_1$, with air gaps between the surfaces of the quartz and the electrodes represented by K_2.

This system has flowing through it a current of which the instantaneous value is represented by i_2. It is shunted across the oscillatory circuit CLR, carrying the current having an instantaneous value i_1. An electromotive force e_0 (assumed constant) is induced in L by very loose coupling to a source of smoothly variable frequency as indicated. A fictitious current i_3 flows in the quartz mesh itself. This cannot be measured, but is introduced for purposes of the algebra of the analysis. It has its counterpart in the physical reaction of the quartz.

The root mean square value of i_1 is measured by heater and thermo-junction connected to galvanometer G_1. Similarly I_2 is measured on G_2. This measurement is difficult owing to the smallness of I_2 and to the smallness of the energy circulating in the shunt system.

When the frequency of the source is smoothly varied through the region of response of the quartz, remarkable changes occur in the values of I_1 and I_2. Owing to the relatively large and sudden absorption of energy by the quartz at the frequency of response the current I_1 falls very rapidly to a very sharply defined minimum, and then rapidly rises again to nearly its previous value. The resonance curve of I_1, which, in the absence of the quartz, assumes a normal shape, has thus a deep and narrow crevasse. This is, of course, well known as a result of the work of Cady and others, and examples are given in his excellent Paper on the subject. The current I_2 rises to a sharp maximum, and suddenly falls to a small value again. The exact form of the curve I_2 and its location with respect to I_1 is, however, considerably dependent upon the conditions under which the experiments are carried out, as will be seen later.

The equations connecting the currents and voltages represented in Fig. 5 are

$$(R+La)i_1+\frac{1}{Ca}(i_1-i_2)=e_0, \qquad \ldots \qquad (1)$$

$$\frac{1}{Ca}(i_2-i_1)+\frac{1}{K_2a}i_2+\frac{1}{K_1a}(i_2-i_3)=0, \qquad \ldots \qquad (2)$$

$$(S+Na+1/Ka)i_3+\frac{1}{K_1a}(i_3-i_2)=0, \qquad \ldots \qquad (3)$$

where a is written for $j\omega$.

Both from an experimental and from a theoretical standpoint it is convenient to calculate I_1 in terms of I_0, when I_0 is the current which is obtained in the oscilla-

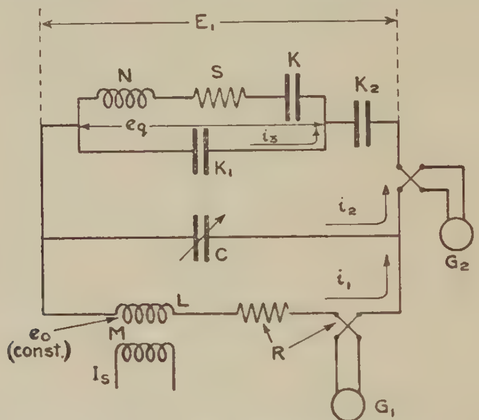

FIG. 5.—CIRCUIT DIAGRAM OF RESONATOR CONNECTED IN PARALLEL WITH AN OSCILLATORY CIRCUIT.

tory circuit when in resonance in the absence of the quartz. We can then write $\sigma_1^2=I_1^2/I_0^2$, where σ_1 is always less than unity.

By elimination of i_3 and i_2 in the above equations and by putting $RI_0=E_0$, where E_0 is the r.m.s. value of e_0 in the final equation for I_1, the expression for σ_1^2 will be found to be

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\left(q+\frac{K(C+K_2)}{CK_t+K_1K_2}\right)^2\right]}{\left[pq+p\frac{K(C+K_2)}{CK_t+K_1K_2}-q\frac{K_1K_2}{CK_t+K_1K_2}-\frac{KK_2}{CK_t+K_1K_2}-\varphi_1\varphi_2\right]^2+\left[q\varphi_1+p\varphi_2+\varphi_1\frac{K(C+K_2)}{CK_t+K_1K_2}-\varphi_2\frac{K_1K_2}{CK_t+K_1K_2}\right]^2} \quad \ldots \quad (4)$$

In order to render the equation more compact the terms

$$\varphi_1=RC\omega, \qquad \varphi_2=SK\omega,$$
$$p=1-LC\omega^2, \qquad q=1-NK\omega^2 \text{ and } K_t=K_1+K_2$$

have been substituted for these respective quantities. It will be remembered that $\varphi_1=\delta_1/\pi$ and $\varphi_2=\delta_2/\pi$, where δ_1 is the log. dec. per complete period of the electrical

circuit LRC, and δ_2 is the log. dec. of the resonator; "q" and "p" are small quantities compared with unity, and to a very close approximation may be considered equal to $\frac{2dn_0}{n_0}$ and $\frac{2dn_1}{n_1}$ respectively, where dn_0 is a small frequency difference from the frequency at which $q=0$ and dn_1 has the same meaning with respect to p.

Now, in the case of quartz, φ_2 is very small indeed—as already anticipated, of the order 30×10^{-6}—and, as a result, σ_1 will assume its minimum value to a very close approximation indeed at that value of q at which the second term in the numerator vanishes—i.e.,

$$q=-\frac{K(C+K_2)}{CK_t+K_1K_2}$$

when σ_1=minimum.

From an experimental standpoint, it is convenient to work in terms of frequency differences, and it is further very desirable to take as datum that frequency at which σ_1 has its minimum value—i.e., the bottom of the crevasse.

The equation can therefore be thrown into this form by substituting a quantity

$$q=-\frac{K(C+K_2)}{CK_t+K_1K_2}-\frac{2dn}{n_0}$$

in place of q.

Equation (4) now becomes, by a further slight simplification,

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\frac{4dn^2}{n^2}\right]}{\left[\frac{2dn}{n_0}\,\frac{K_1K_2}{CK_t+K_1K_2}-p\frac{2dn}{n_0}-\frac{KCK_2^2}{(CK_t+K_1K_2)^2}-\varphi_1\varphi_2\right]^2+\left[p\varphi_2-\frac{2dn}{n_0}\varphi_1-\varphi_2\frac{K_1K_2}{CK_t+K_1K_2}\right]^2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation contains no approximations, and will accurately delineate the curve obtained for any condition of the electric circuit. We still have the term p, which changes rapidly with change of frequency when L and C remain constant, and are so adjusted that $LC\omega^2$ is approximately unity.

When testing the validity of the theorem by experiments, the form taken by equation (5) will depend upon the conditions under which these have been carried out.

A number of cases may arise as follows :—

(*a*) Cady's Experiments.—At each adjustment of frequency to a known value the capacity of the oscillatory circuit is adjusted so that, with respect to this adjustment, σ_1 is a maximum.

This case is met by substituting back into (5) the quantity $I-LC\omega^2$ for "p," and then differentiating with respect to C considered as the variable.

Having thus found an expression for the changes in C from some datum value in terms of dn and the other constants, the quantity $C+dc$ must be substituted back into (5) in order to obtain an equation in which "dn" is the only variable.

A very complicated expression results, which entails tedious computations, and does not lend itself well to the derivation of further equations for the values of $\sigma_{1\min}$.

as a function of the rest of the constants of the circuits when these are varied. A fairly good approximation can be made, as shown later, by consideration of p as the only variable.

This method of experimenting is, moreover, extremely laborious to carry out. A small rate of drift of the source will impair the accuracy of the results, owing to the long time taken to observe a complete curve of σ_1.

(*b*) Another case corresponding somewhat with the above is to adjust the condenser C so that at each frequency $LC\omega^2=1$, i.e., $p=0$.

This case can be carried out fairly easily by disconnection of the resonator from the oscillatory circuit, which is then tuned by adjustment of C to resonance at each frequency adjustment. This setting is best made by a two reading method, since considerable accuracy is necessary.

The observations of σ_1 are now somewhat more quickly made, and in general more accuracy is obtained than by method (*a*). The equation simplifies to

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\frac{4dn^2}{n^2}\right]}{\left[\frac{2dnKK_2}{nCK_t}-\frac{KK_2^2}{CK_t^2}-\varphi_1\varphi_2\right]^2+\left[\frac{2dn\varphi_1}{n}+\frac{K_1K_2\varphi_2}{CK_t}\right]^2} \quad . \quad . \quad . \quad . \quad (6)$$

In this equation CK_t has been used instead of $CK_t+K_1K_2$, since in general the ratio K_1K_2/CK_t is less than 0·005. It will be seen that the equation is simple, and that σ_1 approaches unity rapidly with increasing positive or negative values of "dn."

Another still more convenient method of observation is as follows :—

(*c*) Having adjusted the frequency so that $\sigma_{1\,\text{min.}}$ is obtained, the resonator is disconnected, and C is adjusted so that $LC\omega^2=1$. The maximum value of σ_1 is adjusted to or called unity.

The complete curve of σ_1 against "dn" is then obtained without further adjustment of C. Under these conditions, "p" is equal to $-\frac{2dn}{n}$ for the small frequency changes in question. Equation (5) then takes the form

$$\sigma_1^2=\frac{\varphi_1^2\left[\varphi_2^2+\frac{4dn^2}{n^2}\right]}{\left[\frac{4dn^2}{n^2}+\frac{2dnK_1K_2}{CK_t}-\frac{KK_2^2}{CK^2}-\varphi_1\varphi_2\right]^2+\left[\frac{2dn(\varphi_1+\varphi_2)}{n}+\frac{\varphi_2K_1K_2}{CK_t}\right]^2}. \quad (7)$$

In this equation K_1K_2 has again been neglected in comparison with CK_t.

(*d*) In the more general case, where C is left unvaried, we may set the oscillatory circuit at any frequency near that corresponding to (*a*).

It is convenient to call "Δn" the frequency difference between that at which σ_1 is a minimum—i.e., $q=-\frac{K}{K_t}$, and that at which $LC\omega^2=1$, i.e., $p=0$.

We must then substitute in equation (5) $p=-\frac{2dn}{n}-\frac{2\Delta n}{n}$, where Δn is a small frequency difference which does not vary when n is varied.

The equation for this case becomes

$$\sigma_1^2 = \frac{\varphi_1^2\left[\varphi_2^2 + \frac{4dn^2}{n^2}\right]}{\left[\frac{4dn^2}{n^2} + \frac{2dn}{n}\left(\frac{K_1K_2}{CK_t} + \frac{2\Delta n}{n}\right) - \frac{KK_2^2}{CK^2} - \varphi_1\varphi_2\right]^2 + \left[\frac{2dn(\varphi_1+\varphi_2)}{n} + \varphi_2\left(\frac{K_1K_2}{CK_t} + \frac{2\Delta n}{n}\right)\right]^2} \quad . \quad . \quad . \quad (7a)$$

This equation is useful when it is desired to carry out a series of experiments using various air gaps, as explained later. The frequency of response varies with variation of air gap, as has been shown (Fig. 3). The use of (7*a*) enables us to leave C unchanged notwithstanding the change in response frequency. It is of course necessary to insert the value of Δn appropriate to each observed value of frequency at which $\sigma_{1\text{min.}}$ occurs when the air gap is varied.

In all the equations so far given for σ_1 it will be seen that the crevasse is not symmetrical, since the denominator has values depending upon the sign of "*dn*." For the particular case in which C is so adjusted that $2\Delta n/n = -\frac{K_1K_2}{CK}$ the denominator only contains even powered terms of "*dn*," and hence does not depend upon its sign. For this case, therefore, the crevasse when plotted to a scale of "*dn*" is perfectly symmetrical.

This case is of interest chiefly in connection with determinations of φ_2, since a very simple and accurate expression may be derived from it, as will appear immediately.

In order to be strictly accurate, we should consider φ_1 and φ_2 as variables when "n" is varied, since they contain ω. In practice, however, the range of frequency involved in the interesting part of the curves is so small that, so far as "ω" is concerned, φ_1 and φ_2 may be regarded as constant.

At this stage it is desirable to give some experimental and theoretical examples of curves in order to show the extraordinary accuracy of the agreement which may be obtained and to make clear the effects on the crevasse of varying certain conditions.

In Fig. 6 is an example of a curve of σ_1 for a resonator in the form of a bar approximately 6 cms. ×0·15 cm. ×0·6 cm., vibrating in its fundamental longitudinal mode at a frequency of approximately 44,000 cycles per second.

The case given has been chosen and has been plotted on such a scale as to bring out various points.

The curve has been purposely made unsymmetrical by slightly detuning the electrical circuit, and so corresponds to case (*d*). The electrical circuit is in resonance at a frequency 64 cycles per second lower than the frequency where σ_1 is a minimum.

The flat dotted curve is the curve of current I_0 in the oscillatory circuit that would have been obtained in the absence of the quartz. Owing to the open scale of frequency, the curve loses its more familiar shape, and what usually appear as a sharp peak is now a very rounded top. The whole belt of frequency covered on this curve is 0·5 per cent. wide.

The constants of the circuit and the air gap have been chosen so as to give a very deep crevasse having a minimum value of 0·128.

The curve has not been drawn through the points, but from an equation of the form (7*a*), and the observed points have been very carefully plotted—as dots in circles—afterwards.

It will be seen that the agreement is very striking, and shows that within the accuracy possible experimentally the electrical behaviour of the resonator is exactly represented by the mesh of Fig. 2.

The two parallel dotted lines show a belt of frequency of width of one part in a thousand.

The next sheet of curves, Fig. 7, refers to the same resonator vibrating in the

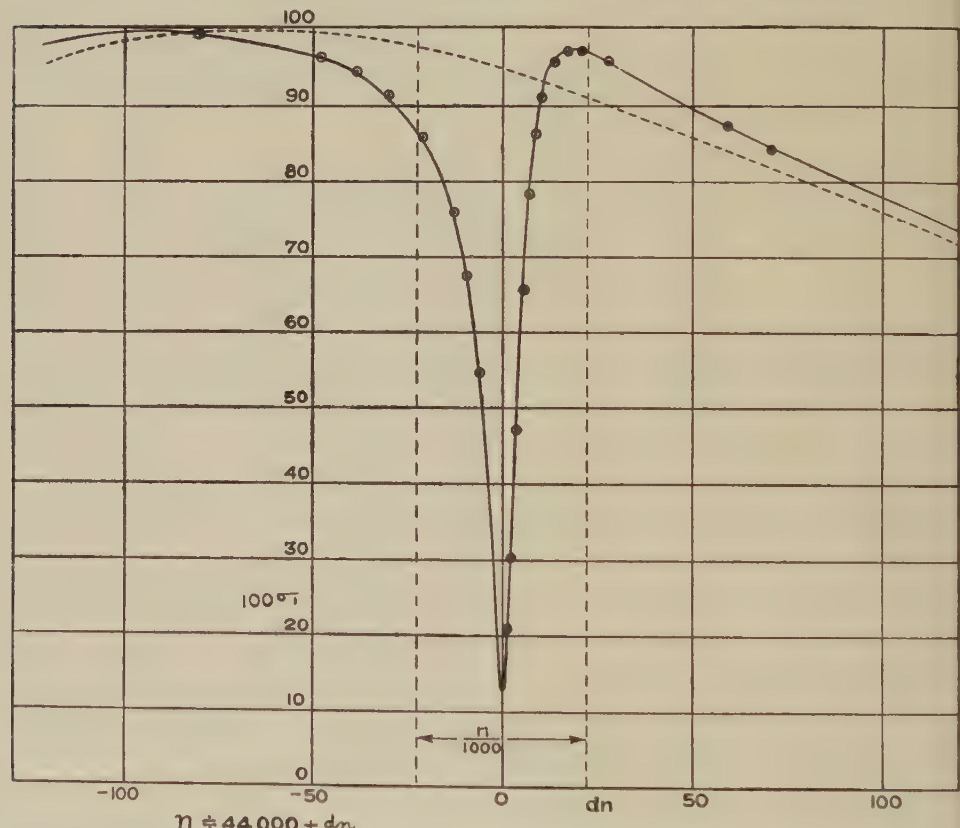

FIG. 6.—RESPONSE CREVASSE IN CURRENT RESONANCE CURVE FOR A LONGITUDINAL RESONATOR.

same mode as in Fig. 6. The air gap is slightly larger, the electrical circuit is such that the minimum is not so small as in the previous case, and the curves have been drawn on a very much more open scale of frequency in order to bring out the shape more clearly. The parallel dotted lines show a belt one part in ten thousand wide. In the case of curve A the circuit has been as nearly as possible experimentally tuned to exact resonance at the frequency of maximum response for a case where the quartz crystal is in position but prevented from vibrating.

This corresponds to equation (7*a*), but the quantity $\frac{2\Delta n}{n}$ has been made equal to $-\frac{K_1K_2}{CK_t}$, so that the curve should theoretically be quite symmetrical. Actually this condition is difficult to adjust quite exactly and so a small term equal to $\frac{K_1K_2}{CK_t}+\frac{2\Delta n}{n}$ has been included so as to fit the experimental curve at two suitable points. The departure from symmetry is inappreciable but can be seen by a close inspection. The curve is again that obtained by the equation and the observed points are again shown by the dots in circles. The equation has been chosen to fit three of the points. The accuracy with which it fits the rest of them shows that the equation rightly accounts for the change in the curve consequent upon changing the electrical circuit.

The other curves are all theoretical and have been drawn to bring out the

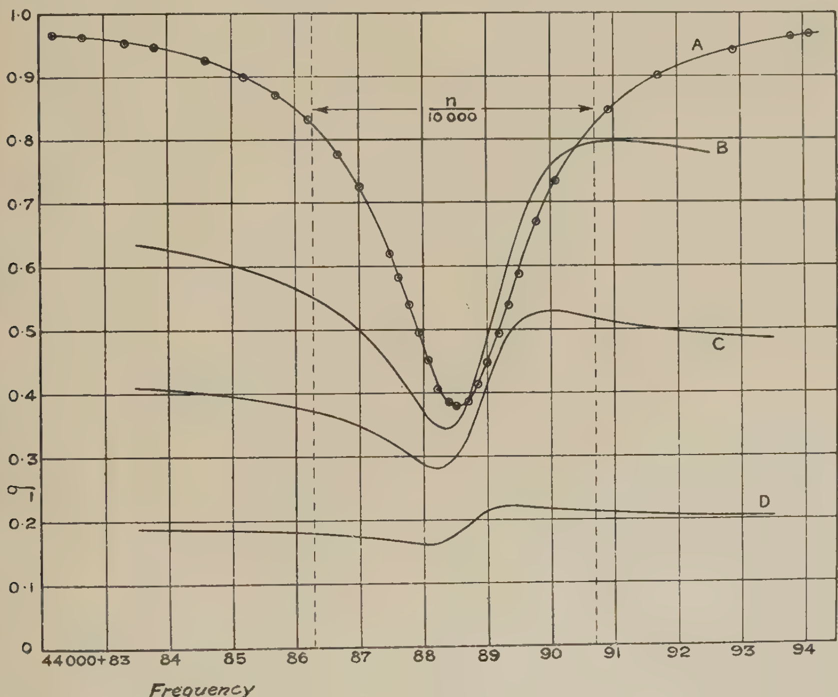

FIG. 7.—RESPONSE CREVASSES SHOWING EFFECT OF DETUNING THE RESONANT CIRCUIT.

effects of detuning the oscillatory circuit. The curves in order B, C and D represent the currents that will be obtained when the circuit is tuned to frequencies 0·5, 1 and 2·5 per cent. respectively, lower than that of curve A. For these cases the crevasse is on the side of the ordinary resonance curve instead of being on the top as at A.

It will be seen that the position of $\sigma_{1\min.}$ is slightly altered as a result of the detuning. In the case of curve B, it is about five parts in a million lower than for curve A, whilst for curve D the crevasse is not well defined and occurs very low down

on one side of the main resonance curve. The minimum here is displaced by about one part in a hundred thousand from that corresponding to the symmetrical curve.

It is thus seen that the frequency at which $\sigma_{1\min.}$ occurs is almost entirely independent of the precise adjustment of the electrical circuit to resonance. The setting of this circuit can, of course, be made much closer to resonance at the desired frequency than 0·5 per cent. Although it is not always easy to set it to one part in ten thousand it can always be set to one part in one thousand. For an uncertainty of this amount the uncertainty of the response frequency of the resonator will not be so great as three parts in a million.

The next curve (Fig. 8) represents a resonator of much higher frequency and of a different type. In this case the resonator is in the form of a small rectangular

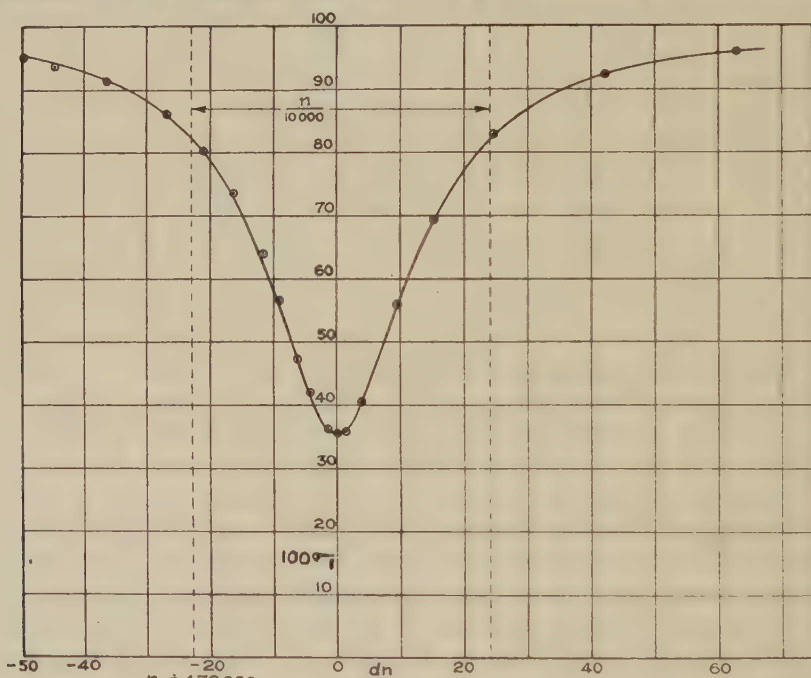

FIG. 8.—RESPONSE CREVASSE FOR A TRANSVERSE RESONATOR.

slab 1·564 cm. × 1·640 cm. × 0·615 cm. thick. This resonator is one which is suitable for the transverse mode of vibration. This particular piece was chosen with special care and is very homogeneous and has a very small logarithmic decrement. It will oscillate readily when suitably connected up with a valve.

The curve corresponds to a nearly symmetrical case. The resonant frequency is approximately 472,000 and the log. dec. is only $0{\cdot}8 \times 10^{-4}$. The main part of the crevasse is comprised within the belt of 1 in 10,000 embraced by the dotted lines.

The remarkable agreement between the observed points (dots in circles) and the calculated curve shows that for a transverse resonator the theory also holds within the experimental limits. The equivalent electrical constants of a given piece of quartz are, of course, quite different according to whether it is vibrating in a longi-

tudinal or in a transverse mode, but in general the log. decs. are about the same and the value of K_1 is not very different for the two modes of vibration.

As might be expected, the damping coefficient for a short high-frequency resonator is not very different from that for a long low-frequency resonator.

As an extreme case, in Fig. 9 is given a curve for a resonator of no less a

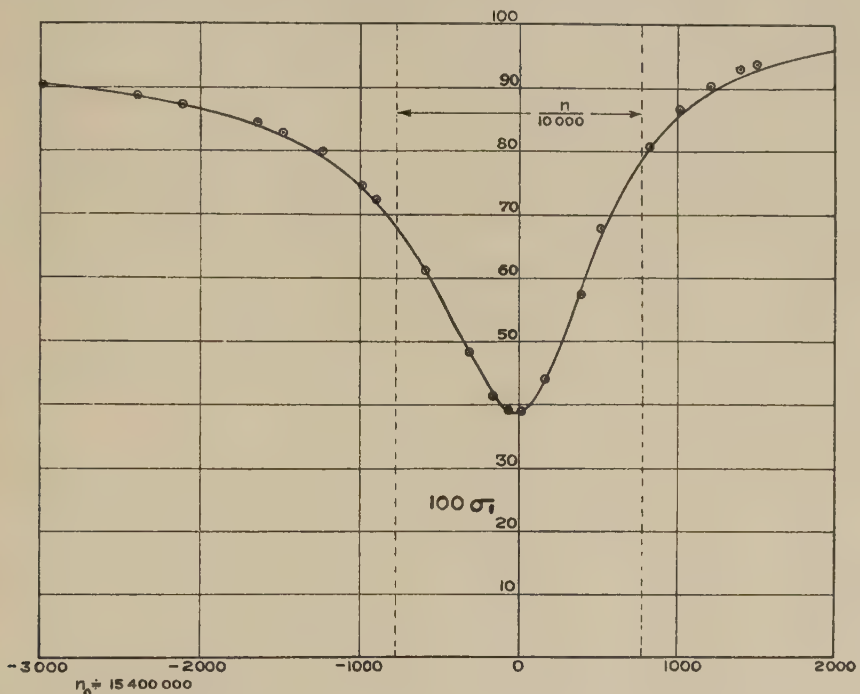

FIG. 9.—RESPONSE CREVASSE FOR A VERY HIGH FREQUENCY TRANSVERSE RESONATOR.

frequency than 15×10^6. This resonator is in the form of a small disc about 0·2 mm. thick and 6 mm. diameter. Its mode of vibration is transverse.

Even at such a frequency the agreement between theory—(drawn curve)—and experiment—(dots in circles)—is satisfactory. In such a case the precise adjustment of the electrical circuit to resonance at the bottom of the crevasse is almost impossible owing to the smallness of the inductance and the capacity. The case shown is one in which the electrical circuit has a resonant frequency somewhat lower than the response frequency of the resonator. The experiments at such frequencies are difficult : special arrangements on the valve oscillator are necessary to enable smooth reversible changes of frequency of uncertainty less than one part in a hundred thousand to be made when the frequency is as high as 15×10^6 (20 metres wavelength).

For all the preceding curves a general form of equation (7*a*) may be used in cases where it is desired merely to plot a curve to see that it fits the points observed. The equation may be written

$$\sigma_1{}^2 = \frac{A^2 + dn^2}{\left[\frac{2dn^2}{n\varphi_1} + Bdn - \frac{A}{\sigma_{1\ \min.}}\right]^2 + \left[dn\left(1 + \frac{2A}{n\varphi_1}\right) + AB\right]^2} \quad . \quad . \quad . \quad . \quad (8)$$

in which $\frac{2}{n\varphi_1}$ belongs only to the electrical circuit, whilst A belongs only to the quartz and is equal to $\frac{n\varphi_2}{2}$. The quantity B depends upon the frequency difference between the electrical circuit and the quartz—whilst $\sigma_{1\text{min.}}$ is determined by the piezo-electric reaction of the quartz upon the electrical circuit.

We have now to consider how we can use equations (7 and 7*a*) and derivations from them in order to evaluate the quantities K, S and K_1.

Determination of $\varphi_2 = SK\omega$.

The quantities which we may vary are (a) ω; (b) $\varphi_1 = RC\omega$ (by addition of resistance in the oscillatory circuit); (c) C; (d) K_2 (by variation of the air gaps). We can observe curves of σ_1, as a function of ω in the way already shown in Figs. 6 to 9 for various known values of φ_1, C and K_2.

By observation of the width of the crevasse in terms of the frequency difference at various chosen values of σ_1 as read off on the plotted curve, we can first determine φ_2 as follows :—

Consider the particular case of (7) when "*dn*"=0. The equation becomes

$$\sigma_1{}^2{}_{\text{min.}} = \frac{\varphi_1{}^2\varphi_2{}^2}{\left[\frac{KK_2{}^2}{CK_t{}^2} + \varphi_1\varphi_2\right]^2 + \left[\frac{K_1K_2\varphi_2}{CK_t}\right]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The second term in the denominator is of very small effect on $\sigma_{1\text{ min.}}$ To a first approximation, therefore, we may neglect it. We can then substitute back into equation (7) the term $\varphi_1\varphi_2/\sigma_{1\text{ min.}}$ in place of $\frac{KK_2{}^2}{CK_t{}^2} + \varphi_1\varphi_2$. By confining the attention to that part of the curve corresponding to values of σ_1 not greater than 0·8, terms containing dn^3 and dn^4 may be entirely neglected. On solving for φ_2 it will be found that

$$\varphi_2 = \frac{2dn\sigma_{1\text{ min.}}}{n}\sqrt{\frac{1-\sigma_1{}^2}{\sigma_1{}^2-\sigma_{\text{min.}}{}^2}}\left\{1+\tfrac{1}{2}\frac{\sigma_1{}^2}{1-\sigma_1{}^2}\cdot\frac{K_2{}^2}{\varphi_1{}^2K_t{}^2}\left(\frac{2K}{C}-\frac{K_1{}^2}{C^2}+\frac{nKK_1K_2}{dnC^2K_t}\right)\right\} \quad . \quad (10)$$

The terms in the round brackets are correction terms.

Now this equation may be written in the form

$$\varphi_2 = f[\sigma_1][dn] - f'[\sigma_1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

in which $f'(\sigma_1)$ is a small quantity compared with $f[\sigma_1][dn]$. But φ_2 is also positive when "*dn*" is negative and has a value, say, "*dn′*." Measuring dn' to the left, therefore, we have

$$\varphi_2 = f[\sigma_1][dn'] + f'[\sigma_1] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

If, therefore, we measure the frequency difference $\delta n = dn + dn'$ right across the crevasse as shown in Fig. 10 at the level, **AB** corresponding to any chosen value of σ_1, we shall have

$$2\varphi_2 = f[\sigma_1][\delta n] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The equation for φ_2 then becomes

$$\varphi_2 = \frac{\delta n \sigma_m}{n}\sqrt{\frac{1-\sigma_1^2}{\sigma_1^2-\sigma_m^2}}\left\{1+\tfrac{1}{2}\frac{\sigma_1^2}{1-\sigma_1^2}\cdot\frac{K_2^2}{\varphi_1^2 K_t^2}\left(\frac{2K}{C}-\frac{K_1^2}{C^2}\right)\right\} \quad . \quad . \quad . \quad (14)$$

In this equation K and K_1 are unknown, but as they only occur in a correction term of the order of 1 per cent. or 2 per cent., we may assume a value for K_1 based on a value of 4 for the dielectric constant of quartz. The quantity K (as yet unknown) can be eliminated by substitution of its equivalent in the approximate form of equation (8). This gives

$$\varphi_2 = \frac{\delta n \sigma_m}{n}\sqrt{\frac{1-\sigma_1^2}{\sigma_1^2-\sigma_m^2}}\left\{1+\tfrac{1}{2}\frac{\sigma_1^2}{\varphi_2(1-\sigma_1^2)}\left(\frac{1-\sigma_m}{\sigma_m}\varphi_1\varphi_2-\frac{K_1^2K_2^2}{2C^2K_t^2}\right)\right\} \quad . \quad . \quad . (15)$$

This equation gives a very accurate measure of φ_2 from observations of δn read off at various values of σ_1 from the curve.

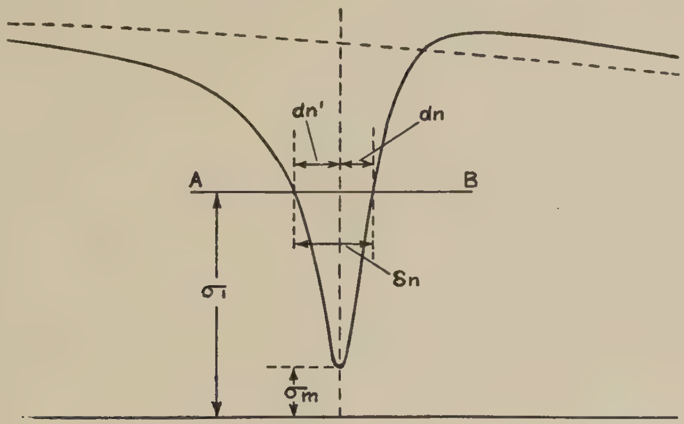

FIG. 10.—DIAGRAMMATIC REPRESENTATION OF A RESPONSE CREVASSE.

For most purposes, however, the correction term may be neglected and the very simple expression (16) used in the determination of φ_2.

$$\varphi_2 = \frac{\delta n \sigma_m}{n}\sqrt{\frac{1-\sigma_1^2}{\sigma_1^2-\sigma_m^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In thus determining φ_2 from a curve, the best way is to read off a series of values of δn corresponding to a number of values of σ_1. By plotting $\sqrt{(\sigma_1^2-\sigma_m^2)/(1-\sigma_1^2)}$ as ordinate to δn as abscissa, a straight line should result of slope "m," such that $\varphi_2 \doteqdot \frac{m\sigma_m}{n}$.

As an example of the determination of φ_2 in this manner, the curve Fig. 11 has been plotted for the case of the curve of which the experimental points are given in Fig. 7. It will be seen that the points lie on a very good line. The value of φ_2 obtained from the line is $29{\cdot}7\times10^{-6}$ whence the logarithmic decrement of the quartz $=\pi\times29{\cdot}7\times10^{-6}=0{\cdot}93\times10^{-4}$.

The measurement of φ_2 constitutes the most important single measurement that can be made on a quartz resonator.

Having determined φ_2 we are in a position to reproduce mathematically any curve for a resonator and a circuit in which φ_1 is known, without further analysis. This is seen from the generalised equation (8) which, except for the quantity B, does not entail any knowledge of the resonator other than its damping. The term B only enters into the equation in so far as it effects the symmetry of the curve. It has been seen already by equation (7a) that B is very largely dependent upon the small difference between the resonant frequencies of the resonator and the electrical circuits. The deduction of B from the asymmetry of the curve cannot, therefore, safely be used for the purpose of further analysing the resonator circuit.

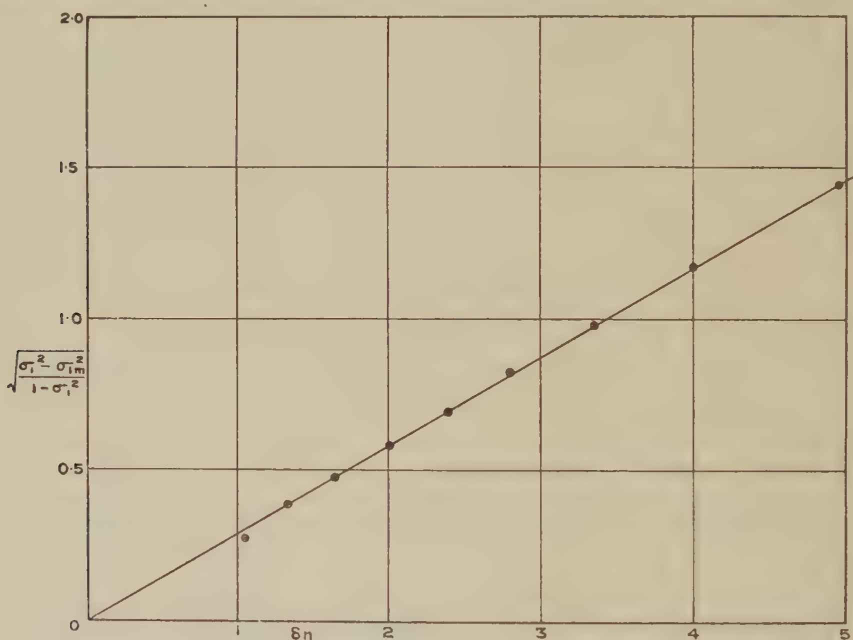

FIG. 11.—LINEAR RELATIONSHIP DEDUCED FROM CREVASSE WHEREBY THE LOG. DEC. OF A RESONATOR MAY BE OBTAINED.

We are therefore left with $\sigma_{1\ \text{min.}}$ only, as a particular property of the observed curve, as a means whereby a further analysis may be made.

Returning to equation (9) in its simplified form, we have, to a close approximation

$$\sigma_{1\ \text{min.}} \doteq \frac{\varphi_1\varphi_2}{\frac{KK_2^2}{CK_t^2}+\varphi_1\varphi_2} \qquad (17)$$

By substitution of $SK\omega$ for φ_2 we can eliminate the unknown quantity K and obtain the equation

$$\sqrt{\frac{\sigma_{1m}}{1-\sigma_{1m}}} = \sqrt{\varphi_1 SC\omega\left(1+\frac{K_1}{K_2}\right)} \qquad (18)$$

The quantities we can vary are :—

K_2 by adjustment of the air gaps to known values.
$\varphi_1 = RC\omega$ by addition of resistance in the oscillatory circuit.
C by choice of capacity and inductance in the oscillatory circuit.

Since C and φ_1 occur in exactly the same way in the equation, nothing is gained by varying more than one of them. In practice it is much easier to vary φ_1, since this does not necessitate retuning and does not react on C.

If a series of curves of σ_1 are taken for various values of K_2, and also with various added resistances in the oscillatory circuit we can observe the following quantities on these curves :—

(*a*) The various values of φ_2.
(*b*) The various values of $\sigma_{1\ \text{min.}}$
(*c*) The frequencies at which the various values of $\sigma_{1\ \text{min.}}$ occur.

Observations (*a*) tell us whether the logarithmic decrement of the resonator is independent of the conditions under which it resonates.

Observations (*c*) will be dealt with later, as they give peculiar results which will repay further investigation.

From observations (*b*) we can find S and K_1 by means of equation (18).

Since φ_2 is also known, we can determine K. Finally, N is determined from the relation $NK\omega^2=1$.

The procedure is to obtain a family of curves each corresponding to a known air gap, and hence known value of K_2. The values of $\sigma_{1\ \text{min.}}$ are then read off. In carrying out these observations it is, of course, not really necessary to obtain the whole of the crevasse, but by way of illustration a family of curves has been taken. Such a family is shown in Fig. 12. These are fairly complete, and enable a number of interesting facts to be seen. In order to avoid confusion, the observed points have been omitted. The curves are experimental, and not theoretical.

Each crevasse corresponds to a particular air gap, and this is the only quantity which has been varied, except for the small change in C necessary to establish resonance in the electrical cfrcuit at each frequency of response.

It will be seen that the frequency of response increases regularly as the air gap is increased, as indicated by the theory represented in Fig. 4. The values of $\sigma_{1\ \text{min.}}$ also lie on a smooth curve representing a reduced effect upon the oscillatory circuit as the air gap is increased.

It has been necessary to draw these curves on a rather compressed scale of frequency owing to the relatively large changes in response frequency with change in air-gap.

From observations made on each curve when drawn on a more open scale the value of φ_2 was deduced.

φ_2 was found to vary somewhat irregularly, as will be seen by reference to the table on Fig. 12, giving this quantity for the various crevasses. There seems to be a slight increase in φ_2 as the air gap is diminished, but this is not regular. It was afterwards found to be due to variations in either the mounting of the resonator or of the humidity of the air.

In a later series only a small portion of the crevasse near $\sigma_{1\ \text{min.}}$ was taken, so that all the necessary observations might be made on one occasion. The mounted resonator was placed in a bell jar and kept dry during this series of observations.

Returning now to equation (18), we can write this in the form

$$\sqrt{\frac{\sigma_{1\ \min.}}{1-\sigma_{1\ \min.}}}=A_1+\frac{A_1K_1}{K_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18a)$$

where $A_1=\sqrt{\varphi_1 SC\omega}=\sqrt{RSC^2\omega^2}$.

It will be seen that on plotting $\sqrt{\frac{\sigma_{1\ \min.}}{1-\sigma_{1\ \min.}}}$ as ordinate against $\frac{1}{K_2}$ as abscissa we should obtain a straight line.

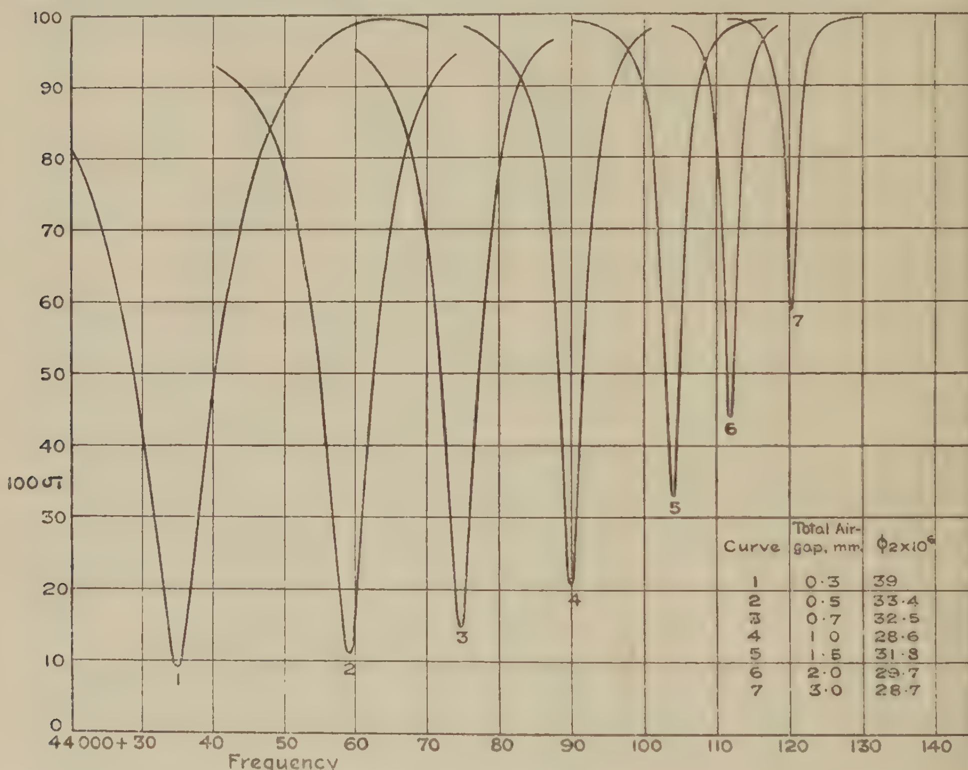

Fig. 12.—Family of Crevasses showing effect of various Air Gaps.

It is obvious from the equation that when $\frac{1}{K_2}$ has the extrapolated imaginary value of $-\frac{1}{K_1}$ the left-hand side of (18) becomes zero. The intersection of the line on the axis of $\frac{1}{K_2}$ gives us therefore $-\frac{1}{K_1}$, and hence K_1.

Again, when $K_2=\infty$, and hence $\frac{1}{K_2}=0$, we have $\sqrt{\frac{\sigma_{1\ \min.}}{1-\sigma_{1\ \min.}}}=A_1$. The intercept of the line on the ordinate axis therefore gives us $A_1=\sqrt{\varphi_1 SC\omega}$. Assuming

that we have measured the effective resistance of the oscillatory circuit, we can calculate φ_1. Of the other terms, C and ω are known, and hence S may be determined.

The slope of the line is equal to A_1K_1. By choosing another value of φ_1—by inserting a known resistance in the oscillatory circuit—another family of curves of σ_1 can be obtained, and from it a second straight line satisfying equation (18) may be deduced. This line should have a slope proportional to $\sqrt{\varphi_1}$, and should confirm by its intercept on the axis of $\frac{1}{K_2}$ the value of $\frac{1}{K_1}$ obtained by the previous line.

A confirmation of both S and K_1 with respect to variation of air gap and of φ_1 may therefore be obtained by observing several series of crevasses, each crevasse in a series corresponding to a known air-gap and each series corresponding to a chosen value of φ_1. The deduced lines of equation (18*a*) should all meet at the point corresponding to $\frac{1}{K_1}$, and their intercepts on the ordinate axis should be proportional to $\sqrt{\varphi_1}$ if S has remained constant.

An overall average value of S may therefore be obtained by plotting the (intercepts)^2 against φ_1, when a line will be obtained whose slope is equal to $SC^2\omega^2$.

An alternative method of dealing with equation (13) when deducing S and K_1 is to consider it in the form

$$\frac{\sigma_{1\ \text{min.}}}{1-\sigma_{1\ \text{min.}}}=RSC^2\omega^2\frac{K_t^2}{K_2^2} \quad \ldots\ldots\ldots\ldots \quad (19)$$

By plotting $\frac{\sigma_{1m}}{1-\sigma_{1m}}$ against R or against " added R " in the oscillatory circuit we can get a series of straight lines each corresponding to a constant value of K_2. These lines should, in the " added R " case, intersect on the axis of—" added R "—at a point $-R_0$, where R_0 is the effective resistance of the oscillatory circuit when " added R "$=0$.

The slopes of the lines are equal to

$$SK_2^2C^2\omega^2/K_t^2=F^2SK_2^2/K_t^2=m_1 \quad \ldots\ldots \quad (20)$$

where $$F=C^2\omega^2.$$

If, therefore, we plot $\sqrt{m_1}$ against $\frac{1}{K_2}$ as before, we shall obtain the intercept giving K_1 and that giving S. The latter does not now involve φ_1, but only C and ω, and the method averages all the observations.

The foregoing methods of analysis have been applied to a number of resonators. The resonator for which the family of curves of σ_1 is shown in Fig. 12 has been completely analysed in this manner.

Three sets of curves similar to those of Fig. 12 were taken for three different total resistances in the oscillatory circuit. The values of $\sqrt{\frac{\sigma_{1m}}{1-\sigma_{1m}}}$ were evaluated in each set at the corresponding values of K_2 and the resulting lines plotted in accordance with equation (18).

These lines are given in Fig. 13. The lines are the best straight lines through the points observed—shown as dots in circles.

A considerable number of points were taken in each case. It will be seen that the points lie on the lines to a good approximation, and that the lines converge with very good agreement to a point of intersection on the abscissa axis.

The data respecting these lines is given in the following table :—

TABLE I.—*Resonator.*

Bar 6·22 cms. long by 0·15 cm. thick (direction of electric axis) by 0·75 cm. deep (optic axis). Vibrating in its fundamental longitudinal mode.

Curve.	Total Resistance in Oscillatory Circuit.	φ_1	Intercept OY	S ohms.	K_1 $\mu\mu F$
A	34·2	$6{\cdot}2 \times 10^{-2}$	0·43	1,650	8·7
B	19·3	$3{\cdot}48 \times 10^{-2}$	0·320	1,635	8·7
C	9·4	$1{\cdot}70 \times 10^{-2}$	0·224	1,640	8·7
D	4·70	$0{\cdot}85 \times 10^{-2}$	0·19	2,360	8·7

It will be seen that in the case of lines A, B, C, the value of S is constant to within less than 1 per cent.

Line D was taken afterwards in order to bring out a special point.

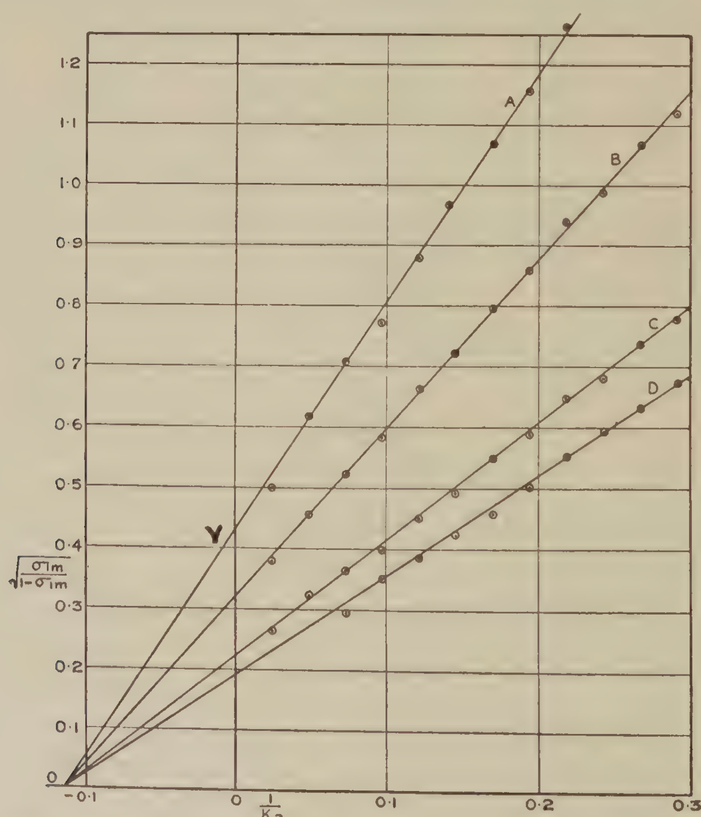

FIG. 13.—LINEAR RELATIONSHIP OBTAINED FROM FIG. 12 WHEREBY THE RESONATOR NETWORK MAY BE ANALYSED.

It was soon found in these experiments that the damping was variable from day to day. This was found to be due to two causes. (*a*) The mode of support, and (*b*) the state of the surface of the resonator with respect to cleanness and dryness.

The experiments resulting in lines A, B and C were very carefully carried out. The resonator, after careful cleaning, was placed in an air-tight enclosure, and dry air was pumped through it after each adjustment had been made to the resonator.

The experiments D were carried out without the enclosure and on a damp day. The increase in S is very marked, and is probably largely due to an increase in the electrical losses on the surface of the quartz. It will be observed that the line passes through the same value of K_1, showing that this constant does not appear to be affected by the moisture in the air.

In order that these particular experiments might be carried through in a single series, attention was concentrated upon observations of $\sigma_{1\,\text{min.}}$, and not on the delineation of the whole of the σ_1 curve. Consequently, values of φ_2 for these actual conditions were not obtained. If, however, the evidence of the tests made in moist air is taken for the purpose of the assumption that K_1 is not dependent on φ_2, we can make use of any of the curves of σ_1 taken at any time notwithstanding φ_2, and hence S may be different for different curves. We can do this, of course, because K_1 may be considered as known and constant in equation (8). For the purpose of obtaining K the equation takes the convenient form

$$K=\varphi_1\varphi_2 C\left(1+\frac{K_1}{K_2}\right)^2\left(\frac{1-\sigma_{1m}}{\sigma_{1m}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Using this equation on about 15 different curves of σ_1 for cases in which φ_1, φ_2 and K_2 have each been varied over wide ranges, results have been obtained as shown in Table II.

TABLE II.—*Longitudinal Resonator—Fundamental Mode of Vibration at* 44,000 $\sim$ *per second. Dimensions*—6·22 *cm. long,* 0·15 *cm. thick,* 0·75 *cm. deep.*

Total Air Gap, mm.	K_2 $\mu\mu F$	φ_1	φ_2	$\sigma_{1\ \text{min.}}$	$K\mu\mu F$
0·3	$13{\cdot}7_3$	$8{\cdot}7\times10^{-3}$	$41{\cdot}0_8\times10^{-6}$	$0{\cdot}09_0$	0·0630
0·3	$13{\cdot}7_3$	$17{\cdot}0\times10^{-3}$	$41{\cdot}0_4\times10^{-6}$	$0{\cdot}17_4$	$0{\cdot}058_1$
0·3	$13{\cdot}7_3$	$8{\cdot}5\times10^{-3}$	$39{\cdot}0_0\times10^{-6}$	$0{\cdot}09_1$	$0{\cdot}057_7$
0·5	$8{\cdot}2_4$	$8{\cdot}5\times10^{-3}$	$33{\cdot}0_4\times10^{-6}$	$0{\cdot}11_0$	$0{\cdot}063_2$
0·5	$8{\cdot}2_4$	$20{\cdot}6\times10^{-3}$	$31{\cdot}0_3\times10^{-6}$	$0{\cdot}19_8$	$0{\cdot}059_5$
0·7	5·8	$8{\cdot}5\times10^{-3}$	$32{\cdot}0_5\times10^{-6}$	$0{\cdot}15_0$	$0{\cdot}062_8$
0·7	5·8	$8{\cdot}7\times10^{-3}$	$40{\cdot}0_3\times10^{-6}$	$0{\cdot}18_6$	$0{\cdot}061_5$
1·0	$4{\cdot}1_2$	$8{\cdot}5\times10^{-3}$	$28{\cdot}0_6\times10^{-6}$	$0{\cdot}20_9$	$0{\cdot}058_2$
1·0	$4{\cdot}1_2$	$8{\cdot}7\times10^{-3}$	$40{\cdot}0_2\times10^{-6}$	$0{\cdot}26_9$	$0{\cdot}060_0$
1·0	$4{\cdot}1_2$	$20{\cdot}6\times10^{-3}$	$27{\cdot}0_2\times10^{-6}$	$0{\cdot}37_0$	$0{\cdot}060_5$
1·5	2·75	$8{\cdot}5\times10^{-3}$	$31{\cdot}8\ \times10^{-6}$	$0{\cdot}33_0$	0·0618
1·5	2·75	$8{\cdot}7\times10^{-3}$	$40{\cdot}6\ \times10^{-6}$	$0{\cdot}40_7$	$0{\cdot}058_3$
2·0	$2{\cdot}0_6$	$8{\cdot}5\times10^{-3}$	$29{\cdot}7\ \times10^{-6}$	$0{\cdot}44_0$	$0{\cdot}057_3$
3·0	1·37	$8{\cdot}5\times10^{-3}$	$28{\cdot}7\ \times10^{-6}$	0·588	0·0602
3·0	1·37	$8{\cdot}7\times10^{-3}$	$44{\cdot}0\ \times10^{-6}$	$0{\cdot}68_3$	$0{\cdot}062_4$
			Average value	... ...	0·0603
	Mean variation from mean = 2·7 per cent.				

The foregoing analysis applies to a longitudinal resonator. It is interesting to see whether the same general agreement with theory may be obtained in the case of a piece of quartz vibrating transversely.

A similar set of experiments was, therefore, carried out on the small rectangular piece for which a specimen curve of σ_1 has been given in Fig. 8.

A suitable gap was constructed from an ordinary 25 mm. micrometer gauge, and a careful series of curves of σ_1 for various air gaps and for various values of φ_1 were taken as before.

As will appear later on, remarkable results are obtained with transversely

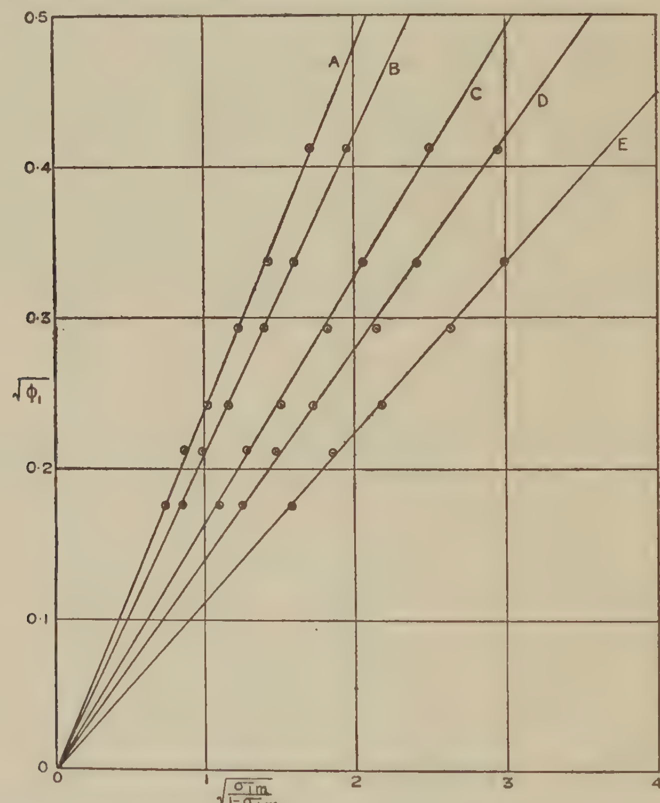

FIG. 14.—LINEAR RELATIONSHIP AS A FUNCTION OF THE LOG. DEC. OF THE OSCILLATORY CIRCUIT.

vibrating resonators under certain adjustments of the air gap. The series of curves was specially chosen in the light of this experience. This explains the apparently irregular air gaps chosen. The results of these experiments are shown in Fig. 14.

By way of variation, the lines have been plotted in accordance with equation (19). Thus, taking square roots of each side, $\sqrt{\sigma_{1m}/1-\sigma_{1m}}$—has been plotted as ordinate to an abscissa which is a fraction of the total resistance in the circuit. Actually the quantity plotted is $\sqrt{\varphi_1}$.

Each line A, B, C, etc., now corresponds to a definite air gap. The points on

the line are obtained from calculation made from the observation of the values of $\sigma_{1\,\text{min.}}$ obtained for various values of added resistance to the oscillatory circuit. By the help of the measurement of the effective resistance of the circuit when no resistance is added the value of φ_1 was calculated in each case.

The lines of Fig. 14 correspond in order to air gaps of 0·2, 0·4, 0·9, 1·2 and 1·8 mm., for which the capacities K_2 are 11·35, 5·67, 2·52, 1·88 and 1·26$\mu\mu$F respectively.

It will be seen that good proportionality exists between φ_1 and $\sigma_{1m}/1-\sigma_{1m}$.

The slopes of these lines gives us a quantity m_2, such that

$$m_2=\sqrt{\sigma_{1m}/\varphi_1(1-\sigma_{1m})}=(1+K_1/K_2)\sqrt{\varphi_2 C/K}.$$

It will be seen that on plotting m_2 against $1/K_2$ we shall get a mean line similar to those of Fig. 13.

The necessary measurement of φ_2 for each air gap was carried out for the condition "added R"=0. The values obtained varied considerably, and appeared to

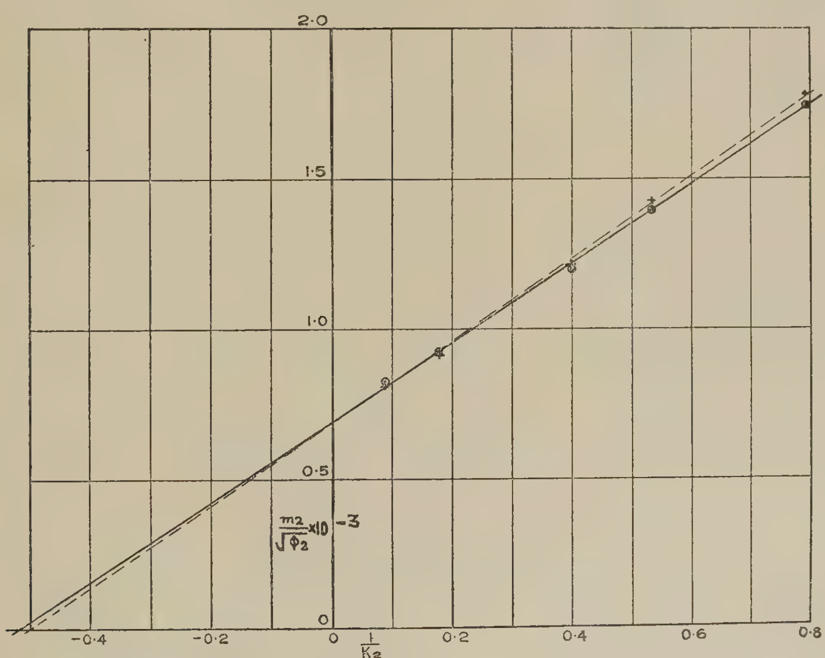

FIG. 15.—ANALYSIS OF RESONATOR NETWORK FROM OBSERVATIONS ON THE LINES OF FIG. 14.

diminish with increasing air gap. In the light of much more careful experiments made to investigate the effects of air gap on damping, remarkable effects were obtained, and for this series of experiments it is probable that an average of the values of φ_2 represents more nearly the truth than the assumption that the values obtained are each correct.

In order of increasing air gap they were φ_2=27·1, 26·7, 25·6, 25·0 and 24·0 $\times 10^{-6}$ in each case.

The line of Fig. 15 represents the values of $m_2/\sqrt{\varphi_2}$ plotted against $1/K_2$. The intercept on the axis $m_2/\sqrt{\varphi_2}$ gives $\sqrt{C/K}$, from which K is determined. The

intercept on the axis of $1/K_2$ gives $-\frac{1}{K_1}$. From the line the actual values are $K=0{\cdot}0041\,\mu\mu\text{F}$ and $K_1=1{\cdot}93\mu\mu\text{F}$. If the observed values of φ_2 are used the dotted line is obtained which appears to be slightly steeper and gives for K and K_1, the values $0{\cdot}0041\,\mu\mu\text{F}$ and $2{\cdot}00\,\mu\mu\text{F}$ respectively.

Effect of Air Gap on Frequency.

We have seen in the simple circle diagram of the resonator that according to the theory the response frequency is a different quantity from what has been defined as the true resonant frequency—i.e., that frequency at which $NK\omega_0^2=1$.

We have seen that the response frequency at which σ_1 has its minimum value occurs to a very close approximation, when the effective capacity K_0 of the resonator mesh is equal to $-K_2$. As already noted in equation (4) this means that $\sigma_{1\text{min.}}$ occurs when $q=-\frac{K}{K_1+K_2}$.

We have, therefore, $1-NK\omega^2 \doteqdot 2(n_0-n)/n_0$ for any value of n near n_0.

This gives the relation

$$n_{[\sigma_{1\text{min.}}]}=n_0+n_0K/2(K_1+K_2), \qquad \ldots \ldots \quad (22)$$

where $n_{[\sigma_{1\text{min.}}]}$ is the frequency at which σ_1 has its minimum value.

By observation of $n_{[\sigma_{1\text{min.}}]}$ at various values of K_2 we ought, therefore, to obtain a check on the value of K or to discover whether K varies slightly with air gap.

Using the determined value of K_1 we can plot $n_{[\sigma_{1\text{min.}}]}$ against $\frac{1}{K_1+K_2}$. A straight line should result having a slope $n_0K/2$, and an intercept, where $\frac{1}{K_1+K_2}=0$, at which point $n=n_0$.

A great number of measurements of the response frequency have been made, on various resonators as a function of air gap, and a number of very interesting results have been obtained.

A typical case is given in the curve of Fig. 16 for the longitudinal resonator of which the analysis has already been given. The values of response frequency are plotted against the corresponding values of $1/(K_1+K_2)$. For this purpose the value $8{\cdot}7\mu\mu\text{F}$ already determined has been used for K_1.

The vertical dotted line represents the case for an infinite air gap, for which $K_2=0$, and hence gives a limiting value beyond which n cannot rise.

A thin line of slope to fit the equation $\frac{2dn}{n}=\frac{K}{K_t}$ has been drawn to pass through the point A on the experimental curve. Values of $0{\cdot}0603\mu\mu\text{F}$ and $8{\cdot}7\mu\mu\text{F}$ respectively have been used for K and K_1 in calculating this line.

It is seen that the frequency change does not accurately obey the simple theory, but that it tends to do so for large air gaps, where it is practically coincident with the line.

Cady has already indicated that a change of resonant frequency of a bar is to to be expected when the air gap is varied, and suggests that this is due to the leakage electric field resulting from the vibration of the bar. The suggestion is that the vibrating bar is analogous to a bar magnet, and that the leakage field reacts upon the modulus of elasticity thus altering the true resonant frequency.

It is probable that this reasoning is true in part, but it is only necessary to assume it in respect of the departure of the experimental values of n from those corresponding to the straight line of slope $Kn_0/2$, and must not be considered as the main cause of the frequency change.

It may be quite definitely stated that, except for very small air gaps (less than

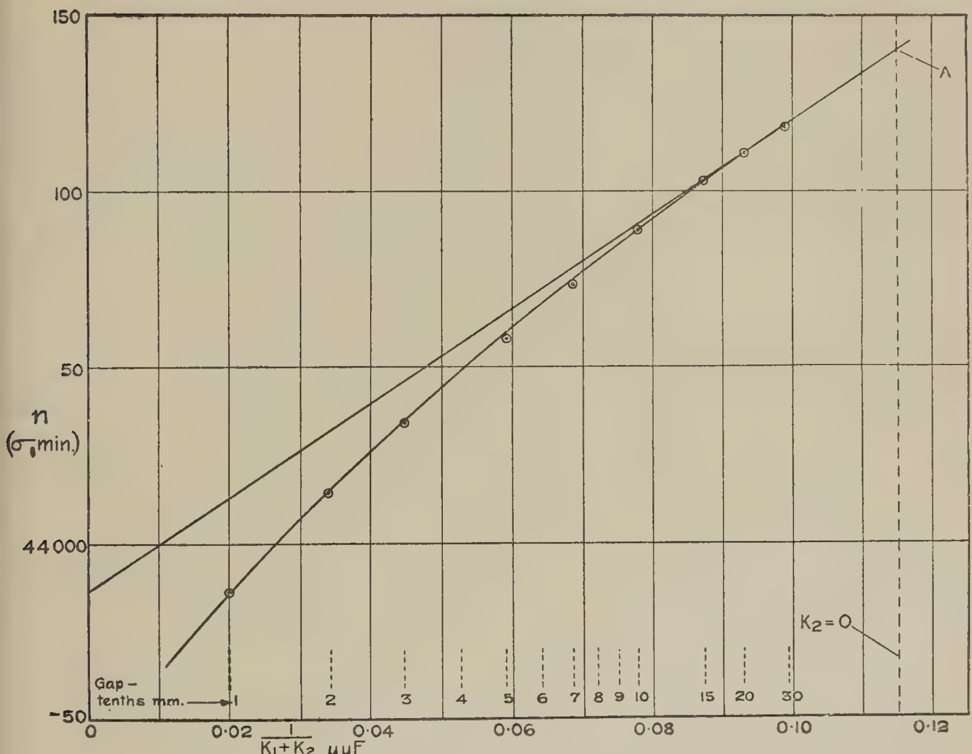

FIG. 16.—VARIATION OF RESPONSE FREQUENCY WITH VARIATION OF AIR GAP FOR A LONGITUDINAL RESONATOR.

0·1 mm.) the main change in frequency consequent upon an alteration in the air-gap is due to the fact that the resonator behaves as an inductance of such value as to give the equivalent electrical resonance corresponding to the capacity K_2 of the air gap.

This is a very interesting fact, and requires further experimenting, using electrodes of smaller length than that of the bar, with a view to the experimental determination of the real change in the true resonant frequency as a function of air gap.

It will be seen that the possible change in frequency is by no means negligible

on a resonator if the air gap changes adventitiously. On the other hand, such a possibility of variation affords a convenient means of finely adjusting the frequency to a desired value when once the resonator has been ground to within one or two parts in a thousand in frequency. There is a range of about three parts in a thousand in a longitudinal resonator for reasonable limits of the air gap.

To a sufficient approximation the change in frequency produced by an increase in air gap from a total of t_1 to t_2 will be given by the expression

$$\frac{\Delta n}{n}=\frac{kt}{2\mu}\left[\frac{t_2-t_1}{(kt_1+t)\,(kt_2+t)}\right]$$

where t is the thickness of the quartz,

k is its dielectric constant (approx. 4·3),

and μ is the piezo-electric ratio K_1/K.

For an average good specimen this quantity is of the order 150 for the transverse effect which produces the longitudinal force. For a good plate vibrating transversely the value of μ is of the order 400 to 500. In the case of a resonator vibrating transversely remarkable effects are obtained when the air gap is varied.

Take, for example, the transverse resonator for which the analysis has been given. For a narrow range of air gap extending from a very small total gap up to one of a few tenths of a millimetre, the change in frequency is smooth and of the same general character as that shown by the longitudinal resonator. The increase in $\sigma_{1\,\text{min.}}$ is also smooth and of the rate to be expected.

At certain air gaps, however, the behaviour is found to be quite rapidly variable. The frequency changes suddenly become negative, and then positive again within quite narrow ranges of air gap. The values of $\sigma_{1\,\text{min.}}$ also show corresponding fluctuations. These effects when first noted strongly suggested further subsidiary resonance phenomena.

Further series of measurements were, therefore, taken with extraordinary care. The micrometer air gap within which the piece of quartz was supported shown in Fig. 32, was found to be uncertain in its action owing to want of parallelness between the plane faces of the electrodes, consequent upon these being not quite perpendicular to the axis of the micrometer screw.

This was a difficult matter to correct, as it is not easy to adjust a plane face 3 cm. in diameter to be so nearly perpendicular to the axis of the micrometer screw that the air gap remains parallel to an accuracy of 0·002 mm. over the whole face for any setting.

After a good deal of adjustment it is believed that this degree of accuracy was attained and the final series of readings was taken.

The readings taken were those of $\sigma_{1\,\text{min.}}$ and frequency for successive changes of 0·02 mm. in air gap on each side over most of the range and for changes of 0·01mm. over certain parts of the range.

The remarkable curves obtained are shown in Figs. 17 and 18. The upper curve gives the variation of frequency with variation in air gap and the lower curve gives the corresponding changes in $\sigma_{1\,\text{min.}}$ Both curves have been plotted to the same scale of air gap and not to a scale of $1/(K_1+K_2)$ as in Fig. 16. The scale represents total air gap, i.e., a reading of 1·0 mm. means that the gap was 0·5 mm. on each side of the resonator. In order to obtain these curves the utmost care was

necessary to ensure that the two air gaps were precisely equal. The equality necessary was certainly to less than 0·01 mm. and was difficult to obtain.

It will be seen that a large increase in the apparent damping and a corresponding

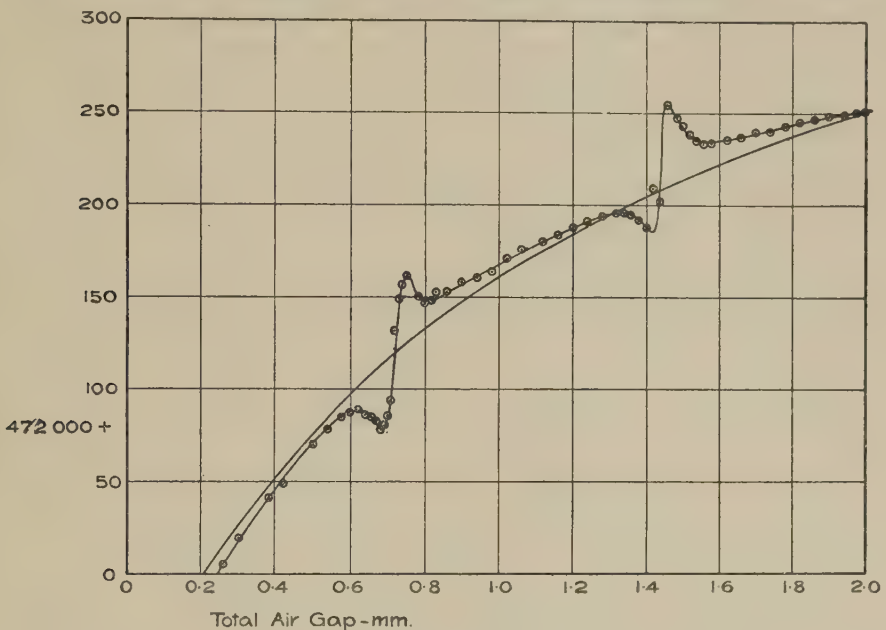

FIG. 17.—VARIATION OF RESPONSE FREQUENCY WITH VARIATION OF AIR GAP FOR A TRANSVERSE RESONATOR.

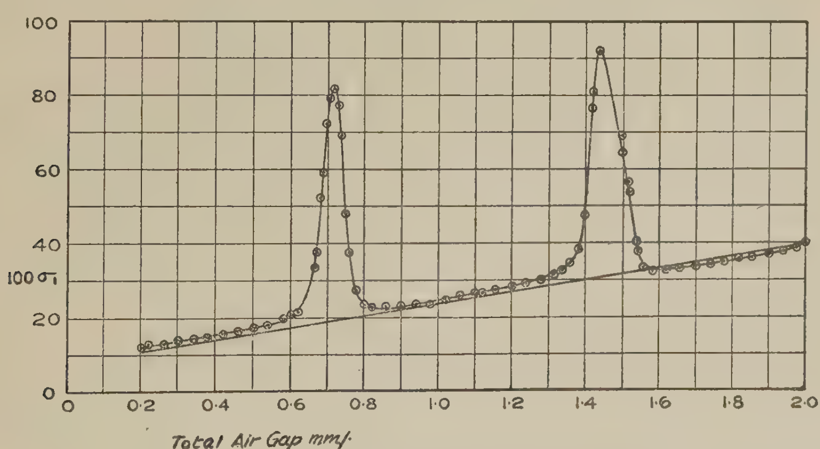

FIG. 18.—VARIATION OF DAMPING COEFFICIENT CORRESPONDING TO FIG. 17.

fluctuation in the frequency of $\sigma_{1\,\mathrm{min.}}$ occurs at air gaps of 0·72 and 1·44 mm., representing gaps on each side of 0·36 and 0·72 mm. respectively.

Now the shape of the two effects suggests immediately to those familiar with

coupled circuits that the equivalent of a coupled resonant circuit is operating. There is no doubt that this is the case and that the effect is due to resonance of the plate of air between the surface of the quartz and the electrode.

The effect recurs every time the air gap has a value which is an integral multiple of the half wavelength of the supersonic air wave corresponding to the frequency of the resonator.

Thus, assuming the value for the velocity of sound in air, of 340 metres per second to hold for such high frequency air waves, then, at a frequency of 472,000 vibrations per second the half wavelength is $\frac{340{,}000}{2\times 472{,}000}=0{\cdot}360$ mm., a result in exact accordance with the observed value.

The damping is enormously increased as a result of the greatly augmented air vibrations occurring in the space between the surface of the quartz and the electrode.

The effective value of φ_2 is increased twenty-fold owing to this large absorption of energy from the quartz. Whether the energy is wasted as viscous damping in the air or whether it is radiated as an augmented air wave I am at present unable to say.

The equivalent electrical system will be that of a closed oscillatory circuit coupled inductively to the fictitious inductance N of Fig. 2.

The thin lines on the figures are the values of $\sigma_{1\,\mathrm{min.}}$ and n respectively, which are obtained by calculation using the previously determined values of S, K and K_1.

Except for the regions where the air resonance introduces its reaction the agreement is quite good in view of the difficulty of the experiments.

It will be seen upon reference to the scale of frequency in Fig. 17 that the change in frequency consequent upon a change in air gap is much smaller for this transverse resonator than for the longitudinal resonator previously given.

The total possible change from zero to an infinite air gap is less than one part in a thousand. The horizontal lines of Fig. 17 are spaced apart roughly by one part in ten thousand in frequency. On the scale upon which these results are plotted, therefore, a change of one part in a hundred thousand in frequency is easily seen.

Within close limits, therefore, it may be provisionally stated that the behaviour of a transverse resonator can be imitated closely by an equivalent electrical network, but that at certain values of air gap the resonator behaves as though an additional resonant circuit were coupled to the network representing the resonator. This resonant circuit nust be considered to have a frequency so varied as to be proportional to K_2 and to become equal to that of the resonator at those values of the air gap, which represent integral half wavelengths in air of the frequency of the resonator.

Current in the Resonator Circuit.

The whole of the preceding considerations refer to the effects upon an oscillatory circuit when the resonator is connected in parallel with the condenser forming the capacity of an oscillatory circuit. It has been shown how an analysis of the network may be made from observations of the current in this circuit.

This procedure, though much favoured by the writer, is by no means the only method by which the equivalent constants of the quartz resonator may be obtained.

We have still to consider the current taken by the resonator itself. This is the current I_2 of Fig. 3(*b*). But there are circuits to which the resonator may be connected other than the oscillatory circuit that we have been considering.

It has already been shown that the circuit representing the resonator itself, is one in which all the parts have very high impedance. Thus, we have K of the order $0{\cdot}05\mu\mu F$ for a resonator of frequency of the order 40,000, $\frac{1}{K\omega}$, therefore, is no less than 80×10^6 ohms. K_2 is of the order $5\mu\mu F$ giving an impedance of about 1 megohm. Measurements on such circuits are by no means easy since the currents are very small except at resonance. It is necessary to use a current measuring device of high resistance in order to obtain useful deflections. The presence of this resistance in the circuit has a considerable effect in reducing the current at resonance and increases the apparent decrement of the resonator considerably. By the use of a Duddell thermo-galvanometer with heater of about 100 ohms it is, however, possible to get observations without risk of breaking the quartz or of vitiating the results owing to reaction on the source. Difficulties also arise owing to parasitic currents to earth since earth capacities are by no means small compared with K, K_1 and K_2.

These effects can, however, all be dealt with by a careful attention to the

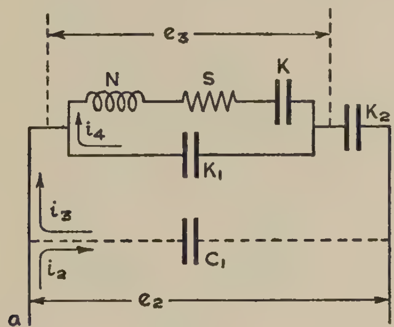

FIG. 19.—DIAGRAM OF THE EQUIVALENT NETWORK OF A RESONATOR CONNECTED TO A CONDENSER.

circuit arrangements and by a correct procedure in the treatment of the observations.

The cases which may be considered are as follows :—

(1) Constant voltage applied to the terminals of the resonator. Two possibilities arise.

(a) The capacity C_1 of Fig. 19 is small but not negligible compared with K_2. Such a capacity always exists in practice due to leads and earth capacities.

(b) The capacity C_1 is purposely made large, by the use of a condenser, but the voltage e_2 is still considered constant (the use of an inducing coil of a very few turns closely coupled to the source enables this condition to be satisfied).

The second case is :—

(2) The voltage e_2 corresponds to that operating when the resonator is shunted across an approximately tuned resonant circuit.

This is the case used experimentally by Cady and is complicated to deal with algebraically.

Cases (1) (a) and (b) will be taken first. The circuit and conditions are as in Fig. 19. The voltage e_2 is to be considered constant.

The instantaneous current i_2 is that of which the root-mean-square value I_2 is measured by the thermo-galvanometer. The current i_3 is to be considered inaccessible to measurement, but its root-mean-square value is a real quantity; i_4 has no existence as a current but has its counterpart in the mechanical vibration of the resonator.

By connexion of the points a, b, to a coil of small self inductance and small resistance so that no approach to resonance in the circuit carrying current i_2 occurs, then, the E.M.F. induced in this coil when coupled to a source will remain sensibly constant over the narrow range of frequency concerned.

Experiments under such conditions show that as frequency is smoothly varied, I_2 rises to a sharply defined maximum then falls to a less well defined minimum, and finally approaches asymptotically its original value. The curve is shown in Fig. 20.

It is convenient, from an experimental standpoint, when C_1 is small, to allow

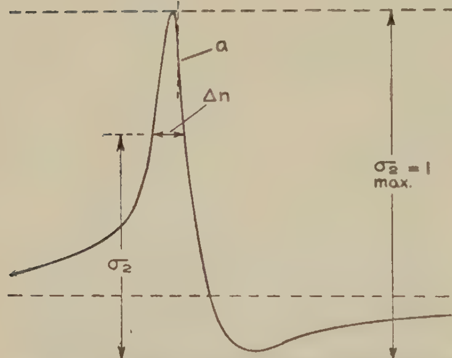

FIG. 20.—CURRENT RESPONSE FREQUENCY CURVE FOR A RESONATOR WITH A SMALL PARASITIC CAPACITY IN PARALLEL.

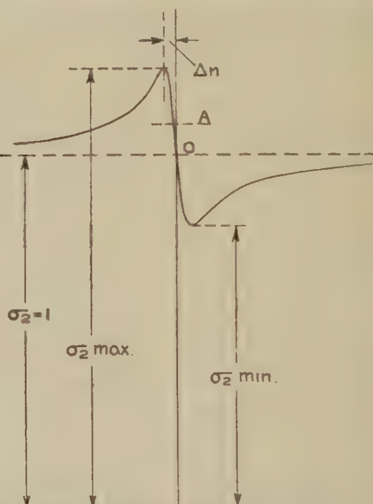

FIG. 21.—THE SAME AS FIG. 20, BUT WITH A RELATIVELY LARGE CAPACITY IN PARALLEL.

the maximum current obtained to be equal to unity and to call the current ratio at any other point σ_2, where $\sigma_2 = I_2/I_{2\,\mathrm{max.}}$.

When C_1 is large, the curve of σ_2 takes on a more symmetrical form of the type shown in Fig. 21. In this case it is more convenient to choose the scale of deflections such that the value of σ_2 approaches unity outside the range where σ_2 changes rapidly. The maximum and minimum values of σ_2 are then connected by the relation $\sigma_{2\mathrm{max.}} \times \sigma_{2\mathrm{min.}} = 1$. The two equations for σ_2 are as follows:—

(a) C_1 small and $\sigma_{2\,\mathrm{max.}}$ chosen equal to unity.

$$\sigma_2^2 = \frac{\varphi_2^2 + \left[q + \dfrac{K(C_1+K_2)}{C_1K_t+K_1K_2}\right]^2}{\left[\varphi_2^2 + \left(q+\dfrac{K}{K_t}\right)^2\right]\left[1 + \dfrac{K^2K_2^4}{K_t^2(C_1K_t+K_1K_2)\varphi_2^2}\right]} \quad . \; . \; . \; . \; . \quad (22)$$

(*b*) C_1 not small, and $\sigma_{2\,\text{max.}} \times \sigma_{2\,\text{min.}} = 1$.

$$\sigma_2^2 = \frac{\varphi_2^2 + \left[q + \dfrac{K(C_1+K_2)}{C_1K_t+K_1K_2} \right]^2}{\varphi_2^2 + (q+K/K_t)^2} \quad \ldots \ldots \quad (23)$$

For certain purposes it is convenient to consider as origin of frequency, that value where $q = -K/K_t$ and to write $q = -\dfrac{K}{K_t} - \dfrac{2dn}{n}$.

Equation (22) becomes

$$\sigma_2^2 = \frac{n^2\varphi_2^2/4 + \left[\dfrac{nKK_2^2}{2K_t(C_1K_t+K_1K_2)} - dn \right]^2}{\left(\dfrac{n^2\varphi_2^2}{4} + dn^2 \right) \left[1 + \dfrac{K^2K_2^4}{\varphi_2^2K_t^2(C_1K_t+K_1K_2)^2} \right]} \quad \ldots \ldots \quad (24)$$

In case (*b*), however, it is more convenient to choose an origin of frequency such that q is the mean of $\dfrac{K(C_1+K_2)}{C_1K_t+K_1K_2}$, and $\dfrac{K}{K_t}$. We substitute for q, therefore, the quantity

$$q = -\frac{K}{2} \left[\frac{(C_1+K_2)}{C_1K_t+K_1K_2} + \frac{1}{K_t} \right] - \frac{2dn}{n}.$$

The equation for σ_2 then takes the very convenient form

$$\sigma_2^2 = \frac{\dfrac{n^2\varphi_2^2}{4} + (D-dn)^2}{\dfrac{n^2\varphi_2^2}{4} + (D+dn)^2} \quad \ldots \ldots \quad (25)$$

where

$$D = \frac{nKK_2^2}{4K_t(C_1K_t+K_1K_2)} \quad \ldots \ldots \quad (25a)$$

These equations differ from those previously considered earlier in the Paper in that the point of resonance is not immediately obvious by an inspection of the curves. If we define resonance as the condition such that the current I_3 actually flowing in the quartz circuit is in phase with the voltage applied, then σ_2 corresponding to this frequency may have values varying from the point a of Fig. 20 very near $\sigma_{2\,\text{max.}}$ for the curve, where C_1 is small to the point A on Fig. 21 very near $\sigma_2 = 1$ for the case where C_1 is large.

We will consider only equation (25) in developing the means of obtaining φ_2 and D.

Differentiating (25) with respect to " dn " for max. and min. values of σ_2 it will be found that $\sigma_{2\,\text{max.}}$ and Δn at which it occurs (*see* Fig. 21) are connected by the equation

$$(\sigma_{2\,\text{max.}})^2 = \frac{2\Delta n/n + \sqrt{4\Delta n^2/n^2 - \varphi_2^2}}{2\Delta n/n - \sqrt{4\Delta n^2/n^2 - \varphi_2^2}} \quad \ldots \ldots \quad (26)$$

From this equation it is found that

$$\varphi_2 = \frac{4\Delta n}{n} \cdot \frac{\sigma_{2\text{max.}}}{\sigma_{2\,\text{max.}}^2 + 1} \quad \ldots \ldots \quad (27)$$

By substitution of φ_2 and $\sigma_{2\,\max.}$ into equation (25) we find that

$$D=\frac{2\Delta n}{n}\cdot\frac{\sigma_2{}^2{}_{\max.}-1}{\sigma_2{}^2{}_{\max.}+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

also

$$D=\frac{\varphi_2(\sigma_2{}^2{}_{\max.}-1)}{2\sigma_{2\max.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

These equations enable φ_2 and the quantity A to be determined from the curve of σ_2.

The determination of K and K_1 can be made by observing a family of curves of σ_2 each corresponding to a chosen air gap and hence known value of K_2.

From these curves, values of A as a function of K_2 may be deduced.

This cannot be done very conveniently for case (*a*) in which C_1 is comparable with K_1, since the base line value of σ_2 is too small to be observed with accuracy. All the curves of σ_2 for various values of K_2 will be nearly similar.

In the case (*b*), however, where C_1 is large compared with K_1 we can write equation (25*a*) for D in the form

$$\frac{1}{\sqrt{D}}=\sqrt{\frac{2C_1}{K}}\left(\frac{K_1}{K_2}+1+\frac{K_1}{2C_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

If, therefore, we plot the experimentally determined values of $\frac{1}{\sqrt{D}}$ obtained by (29) against $\frac{1}{K_2}$ it is seen from equation (30) that a straight line should result from which K and K_1 may be observed.

At the point $\frac{1}{K_2}=0$ the intercept $\frac{1}{\sqrt{D}}$ gives approx. $\sqrt{\frac{2C_1}{K}}$, whence K is determined, since C_1 is known. At the point $\frac{1}{\sqrt{D}}=0$ we have

$$\frac{1}{K_1}=-\left(\frac{1}{K_2}+\frac{1}{2C_1}\right),$$

thus giving K_1, and so analysing the resonator mesh. The measurement of φ_2 by observation of Δn is not very accurate, since this quantity is small, and not too well defined. Also the determination of φ_2 by this relationship only makes use of one point on the curve of σ_2. The curve of σ_2 does not lend itself quite so easily to the development of a straight line of slope proportional to φ_2 in the way already shown for σ_1.

In order to develop such an equation it is convenient and instructive to resort to the vector admittance diagram of the case under consideration—i.e., with the resonator system connected to a condenser across which a constant voltage is maintained.

Fig. 22 gives the vector admittance and conductance relationship for the case concerned. We have already seen that the vector diagram of the simple quartz mesh given by equations (1) and (2) is a circle. A part of this circle has been given

in Fig. 4. Suppose, for the moment, that this impedance circle is that partly shown by the dotted arc passing through O_2 and drawn with O_2X_2 as the axis of effective resistance and O_2Y as axis of effective inductance. We set back O_2O_1 along O_2Y equal to $\frac{1}{K_2\omega}$, and draw an axis O_1X_1, cutting this arc in R. Then O_1R is the effective impedance of the mesh, including K_2 at the frequency of maximum response. Now let us change our scales from those of impedance to those of admittance. The effective impedance O_1R is almost exactly equal to the effective resistance S_1 of Fig. 4, and will become an effective conductance. We can choose the scales so that O_2O_1 now becomes the permittance $K_2\omega$. It is a property of the circular impedance diagram that its inverse admittance diagram is also a circle. This circle is shown as O_2TX_2 of diameter equal to $\frac{1}{O_1R}$. We now set out a new axis ON, such that OO_2 is equal to the permittance $C_1\omega$ of the condenser C_1 of Fig. 6. The circle O_2TX_2 is then redrawn at ONP. The construction of the current-frequency curve $O'N'P'$

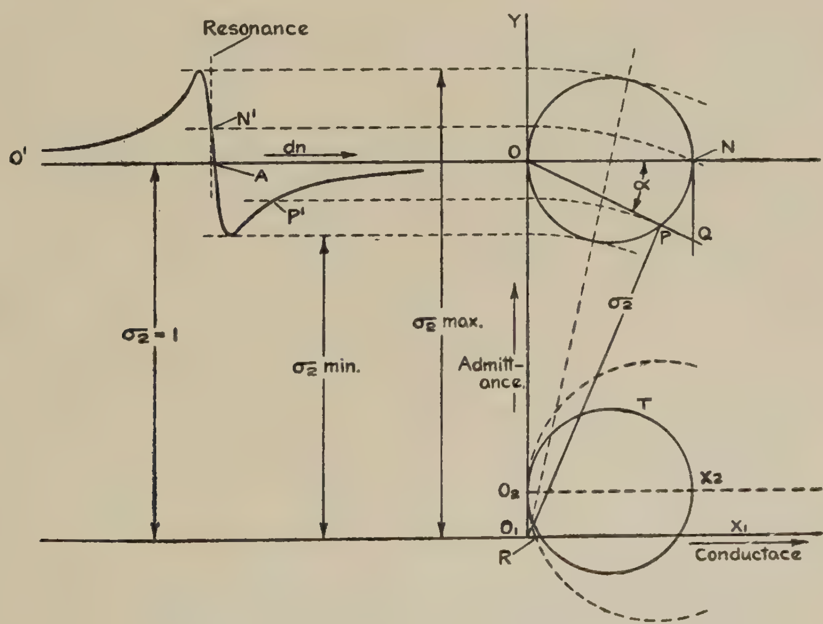

FIG. 22.—GRAPHICAL SOLUTION FOR THE CURVES OF FIGS. 20 AND 21.

follows along lines somewhat similar to those already clearly set out in Prof. Mallett's Paper.(8) In the present case the circle is tangential at O. Any vector admittance O_1P is now shown correctly in phase angle and magnitude with respect to OO_1 for a value of σ_2 corresponding to a point P' on the curve $O'N'P'$ at any chosen frequency difference dn.

Any point P' on the curve $O'N'P'$ of σ_2 has its corresponding point P on the circle ONP. Mallett has shown that the tangent of the angle $\alpha = PON$ is proportional to the frequency difference to which P corresponds from that to which N, the resonant frequency, corresponds.

(The circle is almost completely described for a frequency change of one part in a thousand.)

If we calculate the value of tan α in terms of σ_2 and $\sigma_{2\,\max.}$ by simple trigonometry from Fig. 22 it will be found for the case where we have allowed σ_2 to be unity, as shown in Fig. 22, that tan α is given by the expression

$$1+\tan^2\alpha=\frac{\left(\sigma_{2\max.}-\dfrac{1}{\sigma_{2\max.}}\right)^2}{1+\sigma_2^2\pm\dfrac{2\sigma_{2\max.}}{\sigma_{2\,\max.}^{\,2}-1}\sqrt{(\sigma_{2\,\max.}^{\,2}-\sigma_2^2)\left(\sigma_2^2-\dfrac{1}{\sigma_{2\,\max.}^{\,2}}\right)}} \quad . \quad . \quad . \quad (31)$$

an expression not containing "*dn*." For the case where C_1 is small and $\sigma_{2\max.}$ is chosen equal to unity, the equation becomes

$$1+\tan^2\alpha=\frac{(1+\sigma_b^2)^2}{\sigma_b^2+\sigma_a^2\pm\dfrac{2\sigma_b}{1-\sigma_b^2}\sqrt{(1-\sigma_b^2)(\sigma_2^2-\sigma_b^4)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where σ_b stands for the base line value of σ_2 at frequencies removed from the immediate neighbourhood of response.

Referring back to the circle diagram of Fig. 22, the angle which the admittance vector *OP* makes with *ON* is, of course, the same which the corresponding reactance vector on the dotted reactance circle will make with the resistance axis O_2X_2. Hence, $\tan\alpha=\dfrac{1}{S_0K_0\omega}$, if q in equations (1) and (2) is put equal to $-\dfrac{K}{K_t}-\dfrac{2dn}{n}$. Inserting this value of q into (1) and (2) and calculating $S_0K_0\omega$ therefrom we obtain the very simple relationship

$$\tan\alpha=\frac{2dn}{n}\cdot\frac{1}{\varphi_2},$$

where *dn* is measured from the true response frequency.

On plotting tan α against "*dn*" a straight line should be obtained, the equation of which may be written $n=m\tan\alpha+n_0$, from which $\varphi_2=\dfrac{2m}{n}$, and n_0 is the true response frequency differing very slightly in frequency from the peak in Fig. 20 or from the point *O* in Fig. 21.

In an average satisfactory specimen of quartz this difference is not greater than one part in a hundred thousand. Examples illustrating the cases just considered are shown in Figs. 23 to 26.

The curves refer to the bar vibrating in its lowest longitudinal mode at a frequency of 44,000. The total air gap was 1 mm. Fig. 23 gives the experimental curve of σ_2, obtained for the case where C_1 is only the stray and parasitic earth capacities. The curve is drawn as a heavy line and the points observed are dots in circles.

From observations of "*n*" read off this curve at chosen values of σ_2, and from the calculated values of tan α, using equation (32), corresponding values of tan α and "*n*" have been plotted in Fig. 24. It will be seen that the points lie on a fairly good line, in view of the difficulty in accurately observing such small frequency differences from the curve.

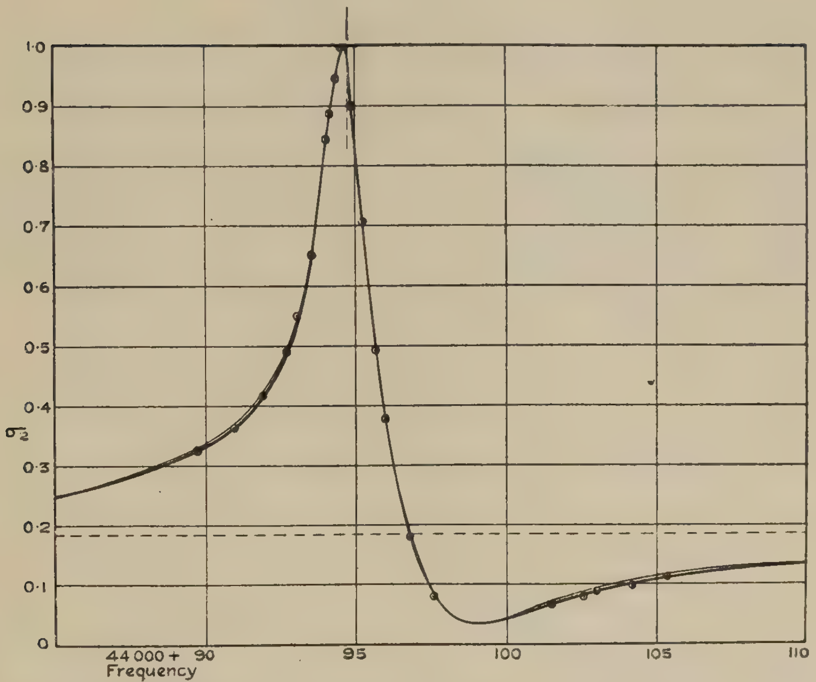

FIG. 23.—EXPERIMENTAL AND CALCULATED CURVES OF THE TYPE AS IN FIG. 20.

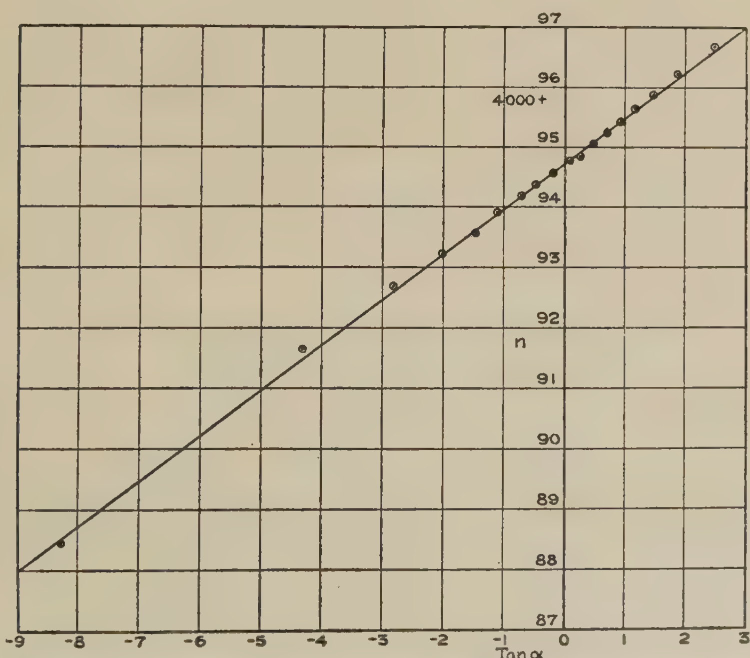

FIG. 24.—LINEAR RELATIONSHIP DEDUCED FROM THE EXPERIMENTAL CURVE OF FIG. 23.

The slope of the line gives the value $34{\cdot}0\times10^{-6}$ for φ_2, which agrees very well with values obtained on other occasions by the other method. The response frequency occurs at $44{,}094{\cdot}7_2$, and is shown by a dotted vertical line on Fig. 23. From this value of φ_2, and from the known value of σ_b, the value of D has been calculated, using the equivalent equation to (29). The curve of σ_2 has then been calculated using equation (25) and multiplying the results by the factor necessary to bring $\sigma_{2\,\mathrm{min.}}=$unity. The curve is shown as a fine line on Fig. 23. The agreement between the observed and the calculated curves is very good. Figs. 25 and 26 show the case of the same bar in the same gap, but the condenser C_1 has been made equal to

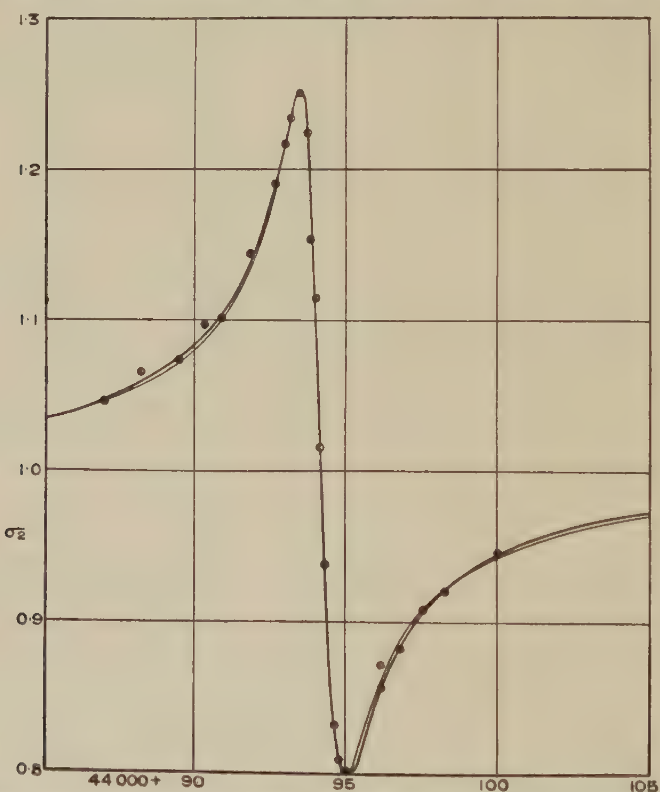

FIG. 25.—EXPERIMENTAL AND CALCULATED RESPONSE CURVES CORRESPONDING TO THE CASE OF FIG. 21.

$350\mu\mu$F. The line of Fig. 26 is fairly good, and the deduced value of $=33{\cdot}7\times10^{-6}$ is in very good agreement with the previous case. The agreement between observed and calculated curves in Fig. 25 is again remarkably good. It will be noticed that the frequency $n_0=44{,}094{\cdot}06$. There is a temperature coefficient of $+12\times10^{-6}$ in the tuning-fork multivibrator, in terms of which the frequencies were measured. The temperature difference of the fork for the two sets of measurements was probably 1°C. in the direction such that the second value 44,094·06 when corrected to the temperature of the first measurement becomes probably $44{,}094{\cdot}5_4$. The two

requencies differ, therefore, by only four parts in a million, which, in view of the fact that the two tests were made on different days, is a very satisfactory agreement.

The further analysis of the resonator by the use of various air gaps has not been carried out, but there is no reason to suppose that complete agreement with the results obtained by the other method would not be obtained. Curves similar to those of Figs. 23 and 25 have been obtained for other sizes of bar and for a plate vibrating transversely.

These experiments, therefore, uphold the equivalent network theory of the resonator, and are in complete accord with those made in the tuned circuit case.

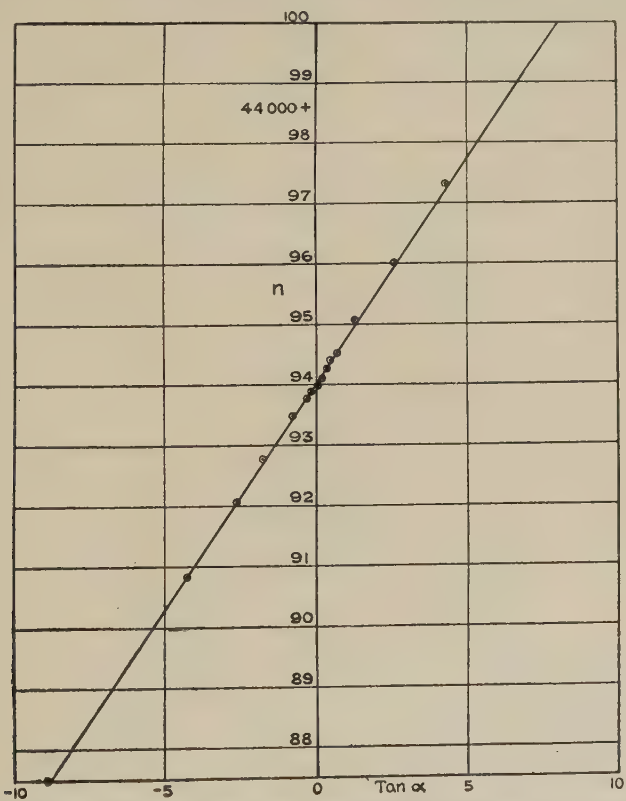

FIG. 26.—LINEAR RELATIONSHIP DEDUCED FROM THE EXPERIMENTAL CURVE OF FIG. 25.

Before bringing this part of the Paper to a conclusion, the case (2) must briefly be considered, in which the current in the branch circuit containing the resonator is measured under the circuit conditions of Fig. 5, in which the resonator is shunted across an oscillatory circuit approximately tuned to the response frequency of the resonator.

If, from the original equations 1, 2, 3, we solve for I_2 in terms of the value to which it tends at frequencies near but outside the belt of response, we can express this as a ratio ρ_2 similar to what has already been considered as σ_2.

The general equation for ρ_2 becomes

$$\rho_2{}^2 = \varphi_1{}^2 \frac{\varphi_2{}^2 + \left[q + \frac{K(C_1+K_2)}{C_1K_t+K_1K_2} \right]^2}{\left[pq + \frac{pK(C+C_1+K_2) - q(C_1K_t+K_1K_2) - K(C_1+K_t)}{CK_t+C_1K_t+K_1K_2} - \varphi_1\varphi_2 \right]^2 + \left[q\varphi_1 + p\varphi_2 + \frac{\varphi_1 K(C+C_1+K_2) - \varphi_2(C_1K_t+K_1K_2)}{CK_t+C_1K_t+K_1K_2} \right]^2} \quad . \quad (33)$$

where all the terms have exactly the same meanings as in previous equations. C_1 is a small parasitic capacity shunting the resonator itself, and includes the capacity of the electrodes outside the quartz, and of the leads to them. This capacity cannot be eliminated, and we cannot measure the true current flowing into the resonator itself.

In the original equation (4) for σ_1 we have not considered the effect of C_1. We are there dealing with the large current flowing through the inductance L. The effect of C_1 upon this is comparatively small, since C_1 is merely a small capacity in parallel with C.

If the full expression for σ_1 is worked out, including the C_1 term, it is found that, in order to express σ_1 in terms of the frequency difference from the bottom of the crevasse, it is necessary to substitute for q the quantity

$$q = -\frac{K(C+C_1+K_2)}{CK_t+C_1K_t+K_1K_2} - \frac{2dn}{n}$$

If this quantity is substituted into the equation for ρ_2 we get

Case I.—C=constant.

$$\frac{\rho_2{}^2}{[C.\ \text{const.}]} = \frac{A^2+(B-dn)^2}{\left[\frac{\varphi_2}{A\varphi_1}\, dn^2 + dn\left(\frac{D}{B}+\frac{2\Delta n}{n\varphi_1}\right) - D + A\right]^2 + \left[dn(1+\varphi_2/\varphi_1) + A\left(\frac{D}{B}+\frac{2\Delta n}{n\varphi_1}\right)\right]^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

in which the following substitutions have been made :—

$$A = \frac{n\varphi_2}{2}; \quad B = \frac{nKCK_2{}^2}{2(C_1K_t+K_1K_2)(CK_t+C_1K_t+K_1K_2)}$$

$$D = \frac{nKCK_2{}^2}{2\varphi_1(CK_t+C_1K_t+K_1K_2)^2}$$

Note B and D have different meanings here from those used earlier in the Paper. In this equation C is constant, and may have any value whatever. The quantity "p" in such a case is best substituted by an expression of the form

$$p = -\frac{2\Delta n}{n} - \frac{2dn}{n},$$

where Δn is a constant frequency difference (generally small), depending upon the

setting of C. It will be remembered that in equation (7a) for σ_1 it was noted that the equivalent term to $\frac{D}{B}+\frac{2\Delta n}{n\varphi_1}$ determined the asymmetry of the σ_1 curve.

Case II.—*LC* circuit adjusted so that at each value of dn, σ_1 is made a maximum

The case, in which C is varied in order that σ_1 may be a maximum, as in Cady's experiments, is complicated to work out accurately, because C appears in so many places in equation (5) for σ_1^2 when the quantity $(1-LC\omega^2)$ is substituted for p. But in many cases we may consider φ_1 and D constant as long as the changes in C are not more than a few per cent.

Under these conditions the only quantity which need be considered as variable, when C is varied, is the quantity "p."

The conditions for σ_1 to be a maximum with respect to variation of C are then reduced to a differentiation of the equation for σ_1^2 with respect to "p" as the variable.

Writing equation (5) in the form

$$\sigma_1^2=\frac{A^2+dn^2}{\left[-\frac{dn}{\varphi_1}p+\frac{D}{B}dn-(D+A)\right]^2+\left[\frac{A}{\varphi_1}p-dn-\frac{AD}{B}\right]^2} \quad . \; . \quad (35)$$

and differentiating with respect to p it will be found that, for σ_1 to be a maximum, p must have the value

$$p=\frac{D\varphi_1}{B}-D\varphi_1\frac{dn}{A^2+dn^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (36)$$

The equations for σ_1 and ρ_2 become, by substitution of p as in (36),

$$\text{Max. } \sigma_1=\frac{A^2+dn^2}{AD+A^2+dn^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (37)$$

$$\text{Max. } \rho_2^2=\frac{(A^2+dn^2)[A^2+(B-dn)^2]}{(AD+A^2+dn^2)^2} \quad . \; . \; . \; . \; . \; . \; . \quad (38)$$

Although we are strictly investigating ρ_2, and not σ_1 when σ_1 is a maximum, the equation for σ_1 is here given. It is seen to represent a symmetrical curve with respect to dn, and, unlike the previous equation for σ_1, equation (37) gives a curve rising asymptotically to unity and never falling again.

Equation (38) has been called ${}_{\text{max.}}\,\rho_2^2$. This is not strictly true when the variation of C is such as to make σ_1 a maximum when the fully accurate case is taken, because C appears in the numerator in the general equation for ρ_2 but is absent in that for σ_1. For all practical purposes, however, the term B in equation (38) may be considered independent of C so long as C is large compared with C_1 and K_1.

This equation represents the peculiar curve given experimentally by Cady. It is seen that when $dn=O$ a sharp minimum occurs on account of the bracket A^2+dn^2, also when $dn=+B$ another minimum occurs. Two maxima occur at values of dn near zero, one positive and the other negative (Fig. 27b).

It remains only to consider the changes in C necessary to satisfy the equation for p.

We may write for p the expression

$$-p=\frac{2dn}{n_0}+\frac{dc}{C_0} \quad \text{. . . . . (39)}$$

where n_0 and C_0 are constant and are related by the equation $4\pi^2 n_0^2 LC_0=1$ and n_0 is the frequency at which $dn=0$.

If this value of p is substituted into equation (36) and, if also, we write $\frac{\Delta C}{C_0}=\frac{dc}{C_0}+\frac{D\varphi_1}{B}$ in order that capacity changes may be measured from the point $dn=0$, it will be found that

$$\frac{\Delta C}{C_0}=D\varphi_1\frac{dn}{A^2+dn^2}-\frac{2dn}{n_0} \quad \text{. . . . . (40)}$$

This equation gives the change in capacity necessary to make a maximum at each chosen value of "*dn*."

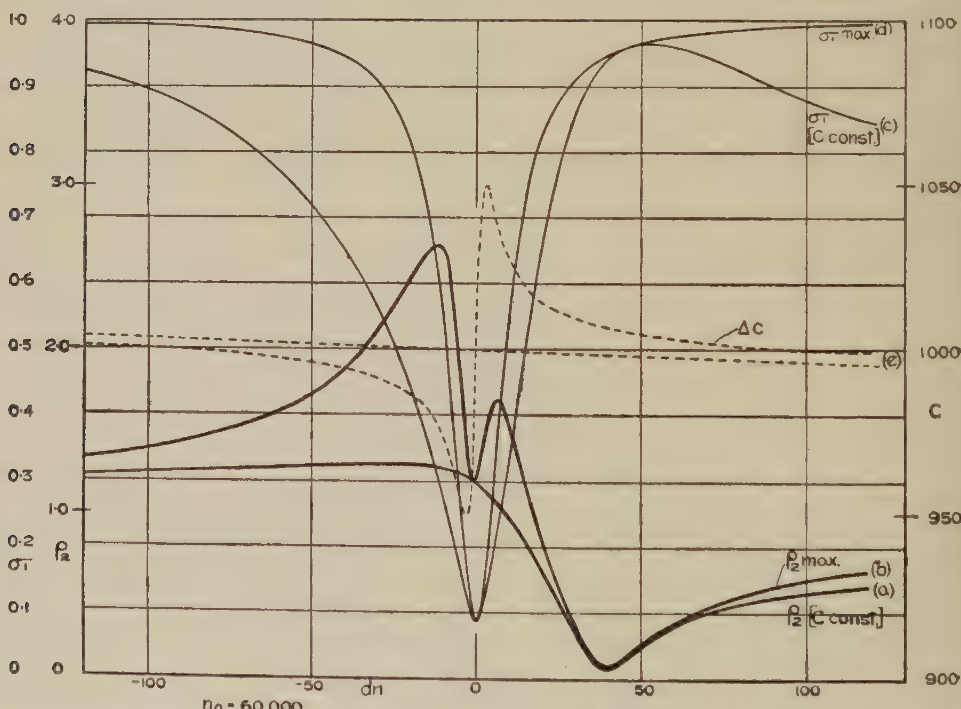

FIG. 27.—GROUP OF CURVES OF σ_1 AND ρ_2 FOR VARIOUS EXPERIMENTAL CONDITIONS OF THE CIRCUIT OF FIG. 5.

As examples of these equations, the set of curves shown in Fig. 27 have been calculated for the following assumed case :—

$$n_0=60{,}000, \quad A=\frac{n\varphi_2}{2}=3, \quad \varphi_2=100\times10^{-6}$$

$$D=30{\cdot}33, \; B=40, \; \varphi_1=1\times10^{-2}, \Delta n=-77{\cdot}5$$

The last term does not enter into the equations for $\sigma_{1\,max.}$ or $\rho_{2\,max.}$ but determines the asymmetry of σ_1. It has been given the arbitrary value of $-77{\cdot}5$ in order to make the curve for σ_1 reasonably but not too unsymmetrical.

The curves which have been drawn are as follows :—

(*a*) ρ_2 when C is constant (equation 33).
(*b*) ρ_2 when C is adjusted so that σ_1 is a maximum (equation 38).
(*c*) σ_1 when C is constant (equation 7*a*).
(*d*) $\sigma_{1\,max.}$ (equation 37).
(*e*) ΔC to satisfy equation (40) using a base line value of 1,000 $\mu\mu$F when $dn=0$.

The similarity of curve (*b*, *d* and *e*) to those observed by Cady will be noted and show that the simple algebraic method of considering the electrical system is substantially in agreement with observation.

A curve similar to (*a*) for a case where C was constant was observed, and gave a curve entirely in agreement in form with that calculated for the above fictitious case.

The equations given for $\varphi_{2\,max.}$ and $\sigma_{1\,max.}$ are only approximate when ΔC is, say, 10 to 20 per cent. of C_0, since all the terms containing C will be considerably changed. If, however, the alternative procedure of changing L were adopted, the equations would become exact and further deductions from them could be made in order to use this means of analysing the resonator mesh. The curve (*e*) would then, of course, be a curve of ΔL, and would be exactly the same in sense and proportions as that for ΔC.

In the example chosen the values of A, B and D are met by choosing the following reasonable electrical quantities :—

$$K_1=K_2=C_1=5\mu\mu\text{F}$$
$$K=0{\cdot}04\ \mu\mu\text{F and } C_0\doteqdot 1{,}000\ \mu\mu\text{F}.$$

The large effect on ρ_2 of the parasitic capacity C_1 of 5 $\mu\mu$F is seen by consideration of B.

If C_1 is neglected

$$B\doteqdot\frac{nKK_2}{2K_1K_t}\doteqdot 120 \text{ cycles per second.}$$

Including C_1 at the assumed value of 5 $\mu\mu$F,

$$B\doteqdot 40 \text{ cycles per second.}$$

Since B represents the frequency difference between the two minimum values of $\rho_{2\,max.}$ and since also the value of $\rho_{2\,max.}$ at $dn=0$ is proportional to B, it is seen that the shape of the curve is very largely dependent upon C_1.

From the equations for $\rho_{2\,max.}$ a series of equations can be developed for the purpose of evaluating φ_2, K and K_1 when using such a method.

This φ_2 becomes given by the equation

$$\varphi_2=\frac{\delta n}{n}\sqrt{\frac{{}_{max.}\sigma_{1\ min.}\,(1-{}_{max.}\sigma_1)}{{}_{max.}\sigma_1-{}_{max.}\sigma_{1\ min.}}}$$

where δn is the frequency difference across the crevasse at a chosen value of $\sigma_{1\,max.}$ Other equations enable D to be obtained for various values of K_2 and φ_1, whereby K and K_1 are determined exactly as already developed.

II. Experimental.

A very great number of resonance curves have been made—two hundred or more—on resonators of all sizes from minute bars only 3 mm. long to bars 120 mm. long and 6 mm. thick ; also on plates and discs from those only 0·2 mm. thick and a few mm. diameter up to a large block 20 mm. thick by 48 mm. by 30 mm. These have been examined not only with respect to their respective fundamental modes of longitudinal and transverse vibration, but also with respect to the overtone modes when the bar is vibrating in 1, 2, 3, etc., up to 9 or more segments. Except in certain very special cases, the electrical equivalent circuit has been found to hold true. The exceptions are those in which two response frequencies are so near together that the crevasses intersect one another.

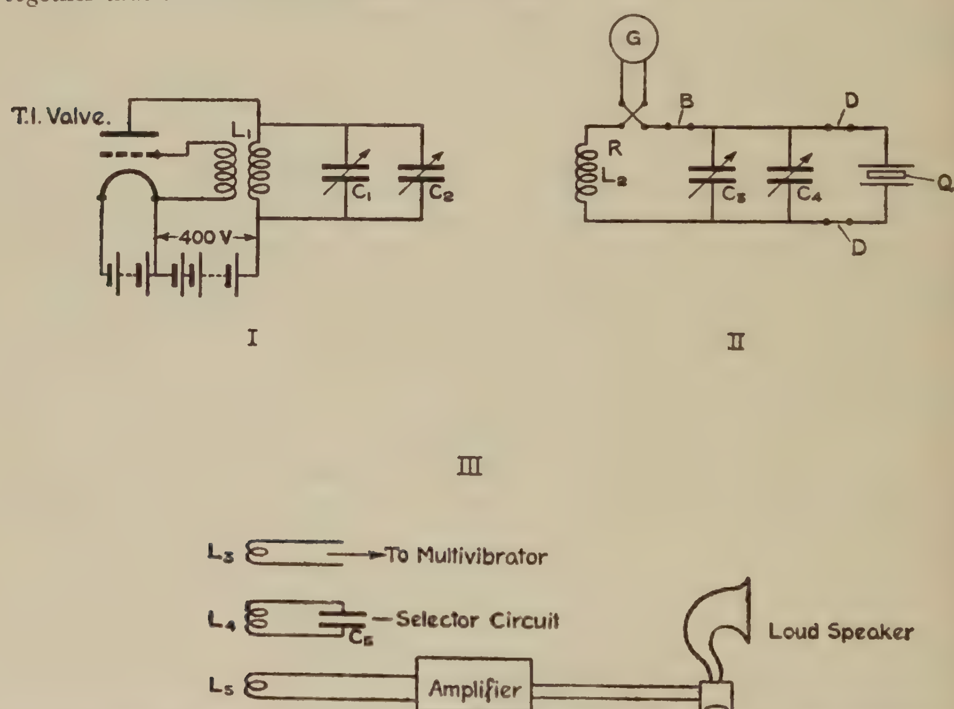

Fig. 28.—Arrangement of Apparatus used in the measurement of σ_1 and Frequency.

Numerous measurements, referred to later, have been made on the temperature coefficient of response frequency and on other effects on frequency and damping not included in the theory.

A very great deal, however, remains to be done in several directions. The subject is one full of interest both from the scientific and practical points of view.

The following information and brief description of the experimental arrangements adopted may, therefore, be of interest.

Measurement of σ_1 and of Frequency.

The apparatus was arranged as in Fig. 28, and consists of three parts :—

(i) The source, in the form of a simple valve oscillator of ordinary type, and not

of the type in which the frequency is controlled by a master valve feeding the grid of a power valve.

It consists of a 250 watt valve, excited from a 400 volt accumulator battery. The inductance and grid coils L_1 are constructed to keep constant in inductance and that coil in the oscillatory circuit is of small log. dec. These qualities are important where it is necessary to reduce the drift of frequency with time to the smallest amount.

The main part of the oscillatory circuit capacity C_1 was in the form of mica condensers of the clamped type. These again are very invariable in capacity with respect to temperature. In general, C_1 was at least 15,000 $\mu\mu$F. C_2 consisted of two variable standard air condensers in parallel, one had a range of about 1,500 $\mu\mu$F and the other was of a much smaller range with an open scale on which a change of 0·1 $\mu\mu$F was easily observed. Sometimes the open range condenser was connected across only a few turns of the inductance coil in order to secure greater openness of the frequency scale. All the condensers were screened in metal cases connected together and to earth. The variable condensers were fitted with long handles to enable precise adjustments to be made from the position at which the galvanometer scale was located.

(ii) The test circuit consisted, in general, of the oscillatory circuit formed by a standard inductance coil L_2 and screened variable air condenser C_3, usually shunted by an open scale small condenser C_4. A vacuum thermo-junction and heater current measurer was inserted where shown and connected to a bifilar galvanometer of good zero-keeping qualities.

A small mercury contact link at B served as a switch and as a gap for the insertion of known standard high-frequency resistance units when so desired.

The quartz resonator mounted in its special gap was connected by thin wires via mercury links DD to the terminals of the condenser C_3. In many cases the resonator was left open to the room, but in others, and particularly in the temperature coefficient measurements, the resonator was placed in a simple electric oven thermostatically controlled in temperature at any desired value up to 50° C. Arrangements were also made to pump dry air into the oven on occasion in order to ensure that moisture did not condense on the quartz on cooling.

The observations made were those of σ_1 at various settings of the Condenser C_2 in the source. The preliminary settings on C_3 and C_4 were first made so that the conditions desired in the test circuit were obtained such as $LC_4\omega^2=1$ when $dn=0$, etc. The coupling was adjusted so that 100 σ_1 on each side of the crevasse was about 99·8 in a normal case, as this was the value found by experience and by calculation to represent the condition $\sigma_0=1{\cdot}000$ in the absence of the resonator.

The adjustments of the condensers C_1 and C_2 were such that C_2 was at about the middle of its scale when σ_1 was at $\sigma_{1\,\text{min.}}$ Readings of σ_1 were then taken at various settings of C_2 suited to the accurate delineation of the curve.

Frequency Measurements.

The arrangements for the measurement of the frequency of $\sigma_{1\,\text{min.}}$ and of the frequency changes corresponding to changes in C_2 were made with very great accuracy by the help of the standard multivibrator wavemeter of the Laboratory.

These arrangements are merely outlined in Fig. 27 as (iii), and the reader is referred to the author's original Paper[(6)] for information regarding the wavemeter itself. It will suffice to say that impulses of exactly known frequency are sent

through a coil L_3 which is loosely coupled to a resonant circuit L_4C_5 of small damping coefficient. The condenser of this circuit is variable and is calibrated in terms of harmonics of the frequency of the impulse current through L_3. By setting the condenser C_5 to the reading corresponding to a chosen harmonic, this frequency is reinforced and interferes with that of the source (i). The two frequencies are received by a selective amplifier tuned to resonance, and after rectification and amplification the telephonic frequency beat note is heard in the loud-speaker.

The multivibrator source is controlled by a valve-maintained tuning-fork. The tuning-fork frequency is so constant that it confers upon the whole system of frequency measurement a most remarkable and unique property which is worthy of mention.

We have, in the wavemeter, the following system. A valve-maintained tuning-fork of frequency adjusted to 1,000·00 cycles per second. This fork, of elinvar steel, has a temperature coefficient of frequency of +12 parts in a million per 1°C. rise in temperature.

This tuning-fork controls a low-frequency multivibrator of 1,000 impulses per second.

All harmonics up to the one hundred and twentieth can be selected from this multivibrator so that a " spectrum " of frequencies up to this limit is obtained by simple selection on the harmonic-selector circuit.

Higher frequencies are obtained by the use of a second multivibrator giving impulses at the rate of 20,000 per second. This multivibrator is kept in harmonic synchronism with the low-frequency one by the intermediary of a fixed-frequency resonant circuit set to 20,000 cycles per second, and a single-valve amplifier.

By the help of additional coils on the selector circuit, harmonics up to about the seventy-fifth can be selected from this multivibrator.

It will be seen therefore that the source can be directly set to any frequency that is an integral number of kilocycles per second up to 120 kc/s by the aid of one multivibrator and to any frequency which is an integral multiple of 20 kc/s up to about 1,500 kc/s. Actually, however, all the intermediate integral kilocycles per second can be successively set and counted round between any two main harmonics such as the thirtieth and the thirty-first on the high-frequency multivibrator giving 600 and 620 kc/s respectively.

Not only can such frequencies be exactly set on the source, but a very great many other subsidiary frequencies may be obtained within the belt of a thousand cycles per second.

Thus, whenever the source has a frequency very close to that represented by the formula

$$n = 1{,}000\left(f \pm \frac{1}{r}\right),$$

where f and r are integers, a slow-synchronization beat is heard. For example, in the case of the resonator of 44,000 cycles per second the following frequencies may be exactly set on the source without any auxiliary apparatus: 44,100, 44,111·1, 44,125, 44,142·8, 44,166·7, etc. With care, further intermediary frequencies can be located between these, such as

$$44{,}125 + \frac{142{\cdot}8 - 125}{1,\ 2,\ 3,\ \text{etc.}}$$

This property of the tuning-fork-controlled multivibrator is quite unique and is only possible on account of the extreme steadiness of frequency of the tuning-fork.

The following table gives a typical set of observations as actually taken on a resonator and shows that it is never necessary to interpolate by more than about two cycles per second from a frequency that is known :—

TABLE III.

Condenser Reading.	Partial Harmonic.	Frequency, 44,000 +	$100\sigma_1$
50			98·4
53·2	$\frac{1}{9}$	111·1	98·0
60			97·7
65			96·7
70			95·6
75			93·75
78·0	$\frac{1}{9 \cdot 333}$	107·2	90·9
81			88·4
84			85·2
87			80·2
89·5	$\frac{1}{9 \cdot 5}$	$105 \cdot 2_5$	73·2
92			65·7
95			56·6
97			44·4
98			34·6
99			$33 \cdot 2_5$
100			$33 \cdot 2_5$
101			34·55
99·5			33·05
102·8	$\frac{1}{9 \cdot 667}$	103·4	36·4
103			40·8
104			44·6
106			58·8
107·6	$\frac{1}{9 \cdot 75}$	102·5	58·8
110			67·2
114			77·2
120			86·3
123·5	$\frac{1}{10}$	100·0	89·4
130			93·0
135			94·8
140	$\frac{1}{10 \cdot 25}$	97·6	96·6
—	$\frac{1}{10 \cdot 5}$	95·2	97·7
—	$\frac{1}{11 \cdot 0}$	90·9	99·1

The frequencies corresponding to the partial harmonics such as $\frac{1{,}000}{9 \cdot 5} = 105 \cdot 2_5$, etc., have been inserted in the table as accurately known frequencies self-determined

by the wavemeter. The other frequencies are obtained by interpolation from a line drawn through these known frequencies when plotted against condenser reading.

It will be seen from the figures that the uncertainties associated with the frequency corresponding to any observed value of C_2 are only of the order 0·1 cycle per second at any part of the curve.

Observations of σ_2.

These were made using a Duddell thermo-galvanometer in which the heater was a thin platinized-quartz rod. The resistance was about 120 ohms and the sensitivity such that full-scale deflection was obtained with a current of about 0·5 milliampere.

In these observations we are dealing with a circuit that is not in resonance, but which is almost a pure capacity. As a consequence the voltage which must be induced is much greater than when a resonant test circuit is used. Closer coupling to the source is therefore necessary for a given energy dissipation in such a case. The changes in frequency are confined to such a narrow belt when observing curves such as those of Figs. 24 and 25 that reaction on the frequency of the source may become troublesome. It is for this reason that it is considered highly desirable to use the resonant-circuit method of determining resonant frequency. A disadvantage of the method whereby the constants of any electrical circuit at radio frequencies are determined by the change in effective reactance rather than in effective resistance is that it becomes almost essential to use a source complicated by the addition of a master-valve oscillator to keep the frequency in the power-valve generator independent of load.

It might be argued that the point of response frequency is defined much more sharply in a curve of the type in Fig. 25 than in one of the crevasse type owing to the fact that one curve runs through the response frequency at a steep angle, whilst the other is the less-well-defined horizontal tangent. In some systems not highly resonant this is true and for such systems the measurement of resonant frequency is best made by the more accurate method. In the case of a quartz resonator the trouble is, not to determine the resonant frequency, but to avoid missing it altogether owing to its extreme sharpness of location. The accuracy of location is extraordinarily great by the method using a resonant circuit. The variations possible in the response frequency due to other causes in the mounted resonator are far greater than any uncertainty due to the method of observation.

Although in the experiments here described the frequencies have been measured with an elaborate and very accurate standard, it is not at all essential to use such a method for the purpose of investigating the equivalent electrical properties of resonators. With the exception of measurements of temperature coefficient and effects which require a considerable time in their determination, the changes in frequency may be observed by simple calibration of the changes in the source when C_2 is varied, using an auxiliary oscillator of frequency which is sensibly constant during the experiments. A second similar quartz oscillator could also be used, of course.

The *temperature* coefficients of frequency of resonators will now be discussed.

Temperature Coefficients of Frequency.

The temperature coefficient of any standard is frequently of vital importance, and in view of the precision obtainable in other respects the variations with temperature of the response frequency of resonators should be known.

Measurements of this quantity were therefore made on a considerable number of resonators and on three oscillators.

Considerable trouble was experienced at first in the measurements owing to the concurrent variations in the air gap with temperature masking the true changes in the response frequency.

These were overcome by the use of suitable mountings for the electrodes, and the careful adjustment of the resonator between them.

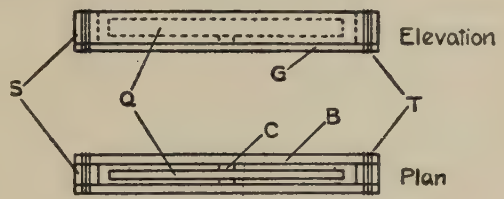

Fig. 29.—Holder for a Longitudinal Resonator for Temp. Coefficient of Frequency Measurements.

For the longitudinal resonators the form of electrodes and the mounting of the resonator were as shown in plan and elevation in Fig. 29.

The electrodes are the narrow brass plates B having their inner faces smooth and flat. These are kept at an accurately known and constant distance apart by small distance pieces of fused silica S, having plane parallel faces. The base consists of a narrow glass slip G, having a small piece of cork C stuck on transversely at the centre of its upper surface. The electrodes with their separators and the glass slip are bound together at each end by silk thread. A narrow trough is thus formed

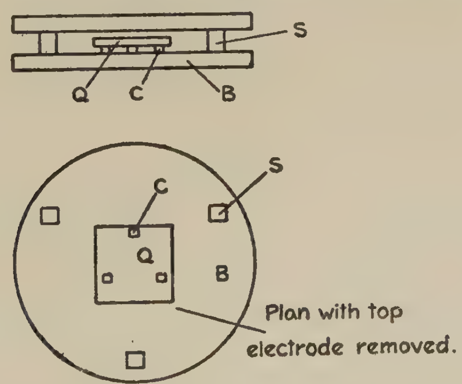

Fig. 30.—Same as Fig. 29, but for a Transverse Resonator.

within which the resonator is centrally balanced on the narrow cork support. Using this form of mounting remarkably consistent results could be obtained notwithstanding the fact that in some cases the temperature coefficient was only 2 or 3 parts in a million per 1°C.

The arrangement for the transverse resonators was the same in principle as that described above, but disc or rectangular shaped electrodes were used. The lower electrode as shown in Fig. 30 was horizontal. Upon this the resonator was rested

on three minute pieces of cork sandpapered to the correct thickness. Three pieces of fused silica of equal thickness with parallel faces served to support the upper electrode.

The mounted specimens were placed in a simple temperature controlled oven, and the response frequencies were measured over a range of temperatures from about 12°C. to about 40°C. Much higher temperatures could have been explored if desired, but for the purpose in view the range given was considered sufficient.

Several longitudinal resonators of various lengths and shapes were measured, and three or four transverse resonators were also observed.

In the use of some of the longitudinal resonators various overtone modes of vibration were measured, since these gave results of considerable interest.

Some complete mounted resonators as made by Messrs. Hilger were also tested, and the author is indebted to them for permission to include these results.

The bars measured had the dimensions as given in the table below :—

TABLE IV.—*Longitudinal Resonators.*

Length in millimetres.

Designation.	Length.	Thickness.	Breadth (along optic axis)
A	47·0	3·3	7·50
B	62·2	1·52	7·54
C	62·5	1·49	7·50
D	9·86	6·72	7·54
E	Hilger Resonators—	Dimensions unknown.	
F	..	..	
	Transverse	*Resonators.*	
G	19·18	2·71	14·61
H	16·42	6·15	14·65
I (disc)	36 mm. diam., 6mm.	thick.	

The results obtained on these bars were as follows :—

TABLE V.

Bar.	Mode of Vibration.	Frequency, cycles per second.	Temp. coeff. parts in a million.	φ_2
A	Fundamental	58,675	$-1{\cdot}0_3$	75×10^{-6}
	Overtone in 3 segments	174,450	$-3{\cdot}0_6$	...
	" " 5 "	273,750	-49	...
	" " 7 "	414,000	-70	...
B	Fundamental	44,120	$-4{\cdot}0_0$	27×10^{-6}
	Overtone in 3 segments	130,850	$-15{\cdot}0_3$	55×10^{-6}
	" " 5 "	219,840	$-5{\cdot}0_2$	$19{\cdot}5 \times 10^{-6}$
	" " 7 "	304,650	-66	22×10^{-6}
C	Fundamental	43,517	$-3{\cdot}0_1$	70×10^{-6}
D	Fundamental longitudinal	413,600	-27	60×10^{-6}
	Fundamental in axis direction	385,260	-51	35×10^{-6}
	Fundamental in axis direction after grinding twined portion away	337,750	-80	47×10^{-6}
E	A. Hilger complete resonators	123,031	Less than 0·2	...
F	" " "	470,800	-16	45×10^{-6}

TABLE VI.—*Transverse Resonators also Usable as Oscillators.*

Bar.	Mode of Vibration.	Frequency, cycles per second.	Temp. coeff. parts in a million.	φ_2
G	Fundamental transverse	847,050	−53	53×10^{-6}
H	,, ,, ...	472,150	−34	22×10^{-6}
I (disc)	Complete mounted crystal in disc form, fundamental transverse	455,500	−26	43×10^{-6}
	Fundamental longitudinal	75,300	−40	47×10^{-6}
	,, ,, in direction of optic axis	106,230	−74	40×10^{-6}

These results are of great interest, but can only be considered fragmentary. Much valuable information would be gained by a complete investigation of the temperature coefficients with special reference to the proportions of length, width and thickness of the bar or plate and with respect to various air gaps.

The ratios of the various frequencies could doubtless be made to yield information regarding the mode of vibration when considered in conjunction with the mathematical theory of resonance in bars or plates. These considerations require a complete investigation in themselves and lie outside the scope of the present Paper.

Returning to the temperature coefficients of frequency it is seen that for the fundamental mode and for the overtone modes in three segments the coefficients are very small.

The coefficients in the direction of the electric axis (transverse mode of vibration) and in the direction of the optic axis (as in disc I) are very much larger.

Measurements of the coefficients of linear expansion and of Young's modulus have been made by various experimenters, and extracts from their results are quoted in a recent Paper by Bragg(4) on the crystal structure of quartz.

I am not at the moment aware that the coefficients of Young's modulus in a transverse plane of the crystal and specifically along and perpendicular to the electric axis under conditions of pure tensile stress in these respective directions have been made, but it would appear that the differences are very great, and that the coefficient of Young's modulus in directions perpendicular to the electric and to the optic axes is smaller than was hitherto supposed.

The method of frequency change is, at any rate, a specially suitable one for the purpose of carrying out such measurements.

The larger coefficients for the higher overtone modes of vibration occur, I think, as a result of the shortness of the vibrating segment. With a segment of length of the same order as the width of the bar the modulus along the crystal axis will exert an influence on the mode of vibration and on the frequency, so that the stresses are no longer even approximately pure, such as will be the case for the fundamental mode of longitudinal vibration of a thin rod, in which a transverse plane section will vibrate with a nearly pure translational motion.

In those cases in which it was observed the value of φ_2 is included in the Table for the various resonators in their various modes of vibration. It will be seen that this quantity varies irregularly with the mode of vibration in the same bar, due, no doubt, to the non-uniformity of the quartz. It is practically impossible to obtain a specimen bar 6 cms. long which is entirely free from visible twinning when examined under the polariscope. If a mixed portion of the bar comes at a node for a particular

mode of vibration it is certain to cause a diminution in amplitude and an increase in the log. dec. of the vibrations. It may be that the anomalous temperature effects in Bar B are associated with the variations in φ_2.

Three conclusions which may be drawn from these measurements of temperature coefficient are :—

(1) That the temperature coefficient of response frequency for a thin bar when vibrating longitudinally is small and in a good specimen is of the order -5×10^{-6} per 1°C. rise in temperature.

(2) The temperature coefficient of response frequency of a disc or plate vibrating transversely in the direction of the electric axis is of the order -40×10^{-6} per 1°C. rise in temperature and is, therefore, by no means negligible. Values ranging from -30 to -70×10^{-6} have been observed.

(3) The temperature coefficient of response frequency of vibration in the direction of the optic axis is larger than either of the foregoing and may reach -80×10^{-6} per 1°C. rise. Also in the case of a disc or plate in which the dimensions along the optic axis and along that axis which is perpendicular to it and to the electric axis, the temperature coefficients of all the modes of vibration are large.

A number of properties of resonators not embraced by the foregoing theory, but nevertheless of importance for design, were investigated and may be summarized shortly in conclusion.

I. Effect on Response Frequency of Displacement of the Resonator from its Position of Centrality in a Fixed Air Gap.

Observations were made of the change in response frequency when a resonator was displaced transversely by successive amounts from the position of centrality within the gap to the position in which one face of the resonator was practically in contact with the electrode. The resonator experimented upon was a bar 62 mm. long, 7·5 mm. deep, and 3·3 mm. thick, the last-named dimension is in the direction of the electric axis.

The observations were only made upon the fundamental longitudinal mode of vibration which had a frequency of about 43·8 kilocycles per second.

The results for two different air gaps are given in the following Table :—

Table VII.

Displacement of Bar, mm.	Frequency Change Parts in 10^6	
	Total Gap 0·7 mm.	Total Gap 2·7 mm.
0	0	0
0·1	−8	−2
0·2	−32	−8
0·3	−80	−18
0·5	...	−44
0·7	...	−78
1·0	...	−153
1·35	...	−284

According to theory, there should, of course, be no change in response frequency whenever the bar is within the gap since the capacity K_2 consists of two condensers

K_a, K_b in series, where a and b are suffixes to identify these capacities with air gaps a and b on either side of the resonator,

$$K_2=\frac{K_aK_b}{K_a+K_b},\quad \text{but } K_a=\frac{B}{A} \text{ and } K_b=\frac{B}{b}$$

where B is a constant.

Hence $$K_2=\frac{B_2/ab}{B/a+B/b}=B/(a+b)=\text{const.}$$

The displacement of the resonator does not alter $a+b$ and hence K_2 does not change. We have already seen, however, by the curve of frequency change (Fig. 16) that the actual change in response frequency is greater than that predicted by theory and that this is probably due to a change in K consequent upon the reaction of the self-induced electric field upon the effective permittivity of the quartz.

It is to be expected, therefore, that the asymmetry of this induced field resulting from the displacement of the resonator will have the effect observed.

Whether the above explanation is correct or whether the cause of the effect is that the electric flux due to the applied field does not remain constant when the resonator is asymmetrical requires further examination. It is, however, quite clear that the effect is by no means negligible from the standpoint of the use of such resonators as frequency standards.

The bar here quoted as an example is relatively thick; in practice the use of a thickness of 3 mm. on a bar 60 mm. long would be considered rather extravagant. With such a bar a possible variation of response frequency of one part in ten thousand can occur if it is mounted with a total gap of 0·7 mm. and no precautions are taken to locate it within the gap. In practice it would be more probable that a thickness of 1·5 mm. would be used for the bar. In such a case a similar frequency range would occur if the total gap were only 0·3 mm. With a smaller gap the total range of frequency due to displacement will be smaller, but on the other hand, the rate of change of frequency is greater. In the case of a bar 1·5 mm. wide with a total air gap of 0·3 mm. the rate of change of frequency with change of air gap would be about +4 parts in a hundred thousand for an increase in air gap of 0·01 mm. A reduction of the air gap to 0·2 mm. would reduce the changes due to asymmetry, but would increase those due to a possible change of 0·01 mm. in the actual gap.

As in so many other cases, the best design is a compromise between conflicting conditions and depends chiefly upon the permissible cost in materials and construction.

Experiments on Oscillators.

Although this Paper deals mainly with the analysis of piezo-electric crystals as resonators because such analysis can be more easily undertaken on resonators than on oscillators a considerable amount of experience has been gained with respect to the behaviour of crystals mounted and used in conjunction with a triode in such a manner as to be self-maintaining. The advantages of such a method of use need no elaboration, their use in such a manner has been described by Cady, Pierce and other experimenters.

With regard to the effects of variation of air gap upon the frequency of maintenance of oscillators a number of experiments made by the author have shown

that the changes are exactly parallel with those obtained on the same specimen when tested as a resonator.

Similarly also with regard to temperature coefficient: this has been found to be the same whether the crystal is tested as an oscillator or as a resonator.

There seems no reason to doubt, therefore, that a similar equivalent electrical network will account for the behaviour of the crystal when functioning as an oscillator as when used as a resonator.

The response frequency as a resonator and the frequency of the self-maintained vibrations as an oscillator are, however, considerably different; in the latter case the frequency is higher so that the crystal considered as a two-terminal piece of apparatus is behaving as a large positive impedance at the self-maintaining frequency. A complete mathematical treatment of the mounted crystal when attached to a valve system is necessary before the significance of this fact can be appreciated. This is not attempted in the present Paper, but the changes in frequency of an oscillator consequent upon the addition of a small capacity across the grid filament circuit suggest that the internal valve capacities are an essential factor in the maintenance of the oscillations and that the grid filament effective input capacity is responsible for the observed frequency difference between resonator and oscillator.

The conditions of operation are, however, more severe for an oscillator. The quartz itself has to be chosen with particular care. In general, a better specimen must be chosen for an oscillator than for a resonator. It must be ground with more care and the faces must be left of a finer matt surface without noticeable scratches. The air gaps have of necessity to be much smaller in order that sufficient reaction on the valve may be obtained to enable it to supply the necessary energy for maintenance of the oscillation. In one simple arrangement the crystal is in the form of a disc or rectangular plate and rests by its own weight on the lower electrode whilst the upper electrode is either lightly pressed upon the upper surface or is otherwise supported, leaving a very small air gap. Observations have shown that considerable variations of frequency are possible—of the order of one part in ten thousand—depending upon the exact condition of the crystal. There appears to be a settling-down or movement into closer apposition with the lower electrode resulting in a slow drift in frequency with time and an increase in the log. dec. of the oscillator so that it is maintained less vigorously in vibration under fixed external conditions. The normal behaviour is usually restored upon turning the mounted crystal upside down and replacing it or by tapping it; it seems necessary that it should "float" on a certain minimum thickness of air in order to operate satisfactorily. I have found that the use of three minute supports for the crystal leaving an air gap of 0·1 mm. results in a satisfactory behaviour.

Considerable difficulties arise in the construction of oscillators for frequencies higher than 3×10^6 cycles per second. The thickness must be uniform to about 0·001 mm. and the proportions of width and length to thickness appear to be of considerable importance. Further investigation on the technical aspect of the production of satisfactory high-frequency oscillators is necessary.

Conclusion and Comments.

1. The conclusions to be drawn from the experiments and simple theory given here would appear to be that an electrical network of the kind first suggested by Butterworth can explain in a general way the behaviour of a piezo-electric resonator

or oscillator. It may be mentioned in passing that before finally using Butterworth's system the writer had developed the system given in Fig. 31 and had found that this system gave a satisfactory explanation of the resonator. It is, in fact, interpretable almost exactly algebraically into the system of Fig. 2. The system actually adopted is, however, somewhat more convenient to use and satisfies the imagination as corresponding more nearly to the physical truth.

With regard to the analysis of the resonator in order to find K, K_1 and S, a matter of considerable theoretical interest, which has purposely been omitted until now, must be mentioned.

An inspection of the equivalent electrical circuit of the resonator shows that at frequencies outside the region where $NK\omega^2$ is nearly unity, the resonator should revert to a simple series circuit consisting of K_1 and K_2 in series, K_2 being the air-gap capacity and K_1 the quartz capacity, calculable from its dimensions and known dielectric constant. It can, of course, be measured also by a direct replacement method at frequencies on each side of the response frequency.

In the case of the longitudinal resonator the calculations and the measurements were made. The value found for K_1 was $11{\cdot}0_7\mu\mu$F, whereas the value at resonance deduced from the crevasses was found to be $8{\cdot}0_7\mu\mu$F. It seems clear, therefore, the effective value of K_1 at resonance is definitely smaller than the geometrical

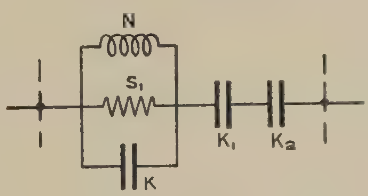

FIG. 31.—ALTERNATIVE EQUIVALENT NETWORK FOR A RESONATOR.

value, as a result of the self-induced electric field. These measurements are difficult, and the probable error in the experimental determinations in the two cases is certainly not less than $0{\cdot}3\mu\mu$F. It is believed, however, that this difference is real. It is interesting to recall in this connexion that in the note in the Phys. Rev. [7] the statement is definitely made there (*see* Ref.[7]) that K_1 at resonance is given by an expression of the form

$$K_1=\left(\frac{K}{4\pi}-\delta\varepsilon\right)\frac{bl}{e}$$

where $\frac{Kbl}{4\pi e}=K_1'$ is the geometric capacity and $\delta\varepsilon\frac{bl}{e}$ is a capacity resulting from the reaction of the electric field upon K.

It is interesting to find that the difference observed is in the direction predicted by the theory of Van Dyke, but the amount found in the experiments described here is much greater than the 1 per cent. found for a resonator of Cady's.

It is probable that the term $\delta\varepsilon$, which is given for the case in which the electrodes are in contact with the quartz, will be multiplied by a considerable factor when there is an air gap, since under these latter conditions the voltage gradient in the quartz is enormously increased.

Thus we have seen, from equation (*a*) and Fig. 4, that the resonator behaves at the response frequency almost exactly as a non-inductive resistance of value $S\frac{K_t^2}{K_2^2}$ by substitution of $-\frac{K}{K_t}$ for q. In a case where $K_1=K_2$ the effective resistance becomes $4S$.

The r.m.s. current I_3 taken by the resonator will be $E_2/4S$, where E_2 is the r.m.s. voltage applied to the terminals. But the voltage across K_2 will be given by $I_3/K_2\omega$; hence the ratio of these voltages is, in the case taken, equal to

$$\frac{1}{4SK_2\omega}=\frac{1}{\varphi_2}\,\frac{K}{4K_2}$$

Assuming normal values of 0·001 for $K/4K_2$, and 30×10^{-6} for φ_2, the ratio of voltages becomes 30. The average r.m.s. voltage across the air gaps is therefore about 30 times that applied to the electrodes. This fact has been used in a beautiful manner by Giebe by placing the mounted resonator in a vacuum so that a visible glow occurs in the air space when the response occurs. The mean r.m.s. voltage across the quartz will therefore also be about 30 times the applied voltage. The gradient over the middle portion of the bar will be considerably greater than that towards the ends.

The voltage gradient is a maximum at the centre of the bar, and has approximately a sine wave distribution from the centre to the ends.

In the case of the transverse resonator completely analysed, the similar measurements at frequencies on each side of the response frequency were made. In this case, however, the statical capacity found for K_1 was 1·6$\mu\mu$F, whereas the vibrational capacity found was 1·9$_3\mu\mu$F, so that the difference here is reversed in sign. Cady does not state whether the vibrational capacity K_1 should be greater or less than the statical K_1' for a resonator vibrating transversely in the form of a plate under the longitudinal piezo-electric effect. The measurements in the case of the small transverse resonator here investigated are, however, even more uncertain than those on the longitudinal resonator, owing to its shape. No great weight can therefore be attached to this difference.

With regard to the calculation of K_1' and K_2, also from the area of the quartz and from the air gap, it may be objected that it is not justifiable to do this using the simple formula on the assumption of an undisturbed electric field. It is realised that to a considerable extent this is true, but at the smaller air gaps the effect will be very small, and at the larger air gaps K_2 has a value which is small compared with K_1', and does not exert much influence on the behaviour. In any case, the straightness of the lines deduced from observations of $\sigma_{1\,\text{min.}}$ with various air gaps and with various values of φ_1, is undoubted, so that the question of an error in K_2 then really resolves itself into a question of units—viz., that K, K_1 and K_2 are all in the same units, but that these may not be strictly $\mu\mu$F units, but that the units are such that by calculating from the simple capacity formula the behaviour of the resonator is consistently explained when used on an external circuit in which the units of capacity is the $\mu\mu$F.

Further work is needed on resonators of larger capacity in order to elucidate the departures of the behaviour of the resonator from the predictions of the theory, in particular in respect of K_1, which is definitely different from its value at

frequencies outside the belt of response owing to the self-induced electric field. In this respect it is probable that as found at the point of maximum response, K_1 really increases from this value to nearly its geometric value as the value of σ_1 rises to unity on each side of the crevasse.

This change cannot easily be elucidated from the curves of σ_1 or σ_2, since K_1 is of comparatively small influence on the shape of these curves.

The reaction of the self-induced electric field on K acting as a cause of

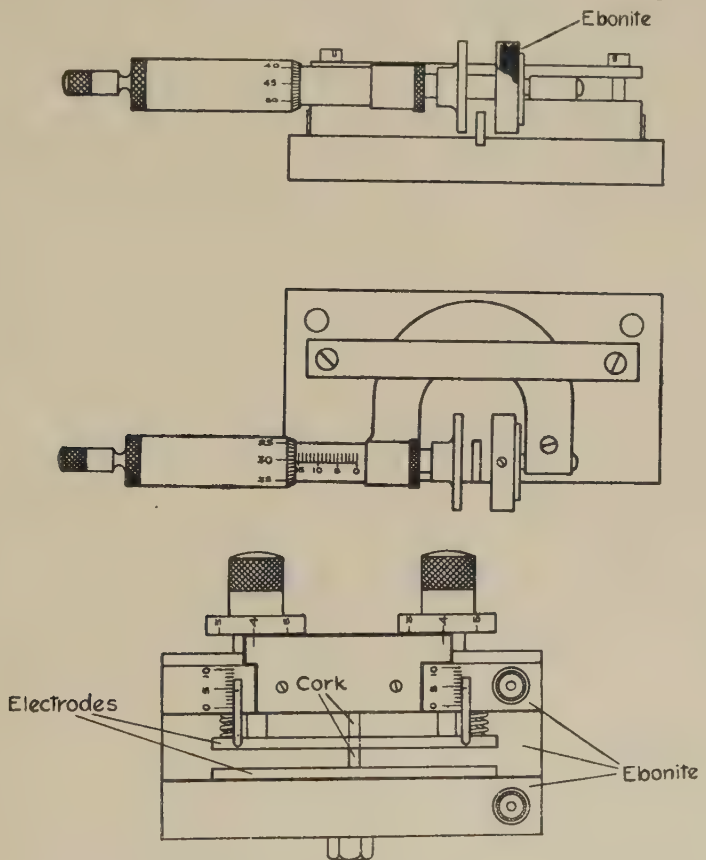

FIG. 32.—ADJUSTABLE AIR GAPS FOR OBSERVATIONS ON RESONATORS WITH VARIOUS VALUES OF K_2.

departure of the response frequency change from that given by theory will also repay further investigation.

In connexion with such more complete investigations, the use of a separate small variable air condenser in series with the resonator has not been overlooked as an alternative to varying K_2. Considerable constructional and experimental difficulties arise, however. The construction of a screened variable condenser which can be varied from about $2\mu\mu$F to $20\mu\mu$F does not appear to have been solved. The high insulation resistance and small dielectric loss necessary, if useful deter-

minations of φ_2 and $\sigma_{1\ min.}$ are to be made, will probably give great difficulty. This avenue would, however, certainly be a useful one to pursue, as it would be possible to work with a fixed known air gap, and so keep all the resonator constants invariable when the series capacity is varied.

2. The temperature coefficients of response frequency are not negligible except for longitudinal resonators of suitable shape. The coefficients are those to be anticipated from the known coefficients of Young's modulus with temperature. Further information regarding the latter could be obtained by a systematic investigation of the frequency temperature coefficients of resonators of various types and modes of vibration. Care would be needed to discriminate a possible effect due to a change in K_1 with temperature. Observations of the coefficients with the same resonator in different air gaps would serve this end.

3. The simple theory developed accounts for those effects on oscillators which are common to resonators ; it is probable that a more complete theory introducing the electrical equivalents of the valve and other associated electrical circuits would account for the further effects on frequency of oscillators consequent upon these circuits. Such effects have been studied to some extent, and are being pursued. Scope for considerable investigation exists in the case of oscillators both from the theoretical and from the experimental points of view.

A considerable future awaits development in the application of resonators and oscillators as frequency standards, filters, frequency controllers, etc. This use at transmitting stations conjointly with the production of local heterodyne frequencies by them will permit of the production of an extremely constant frequency difference. This is an application that has considerable possibilities not yet developed.

In conclusion, I wish to render thanks to Mr. Vigoureux and to Mr. Martin, who have shown much care and patience in taking many of the observations, some of which are tedious. The former has also shown much insight into the experiments, and the latter has prepared some of the specimens with skill.

The work was carried out under the auspices of the Standards Sub-Committee of the Radio Research Board, Department of Scientific and Industrial Research.

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See also :—

An International Comparison of Radio Wavelength Standards by Means of Piezo-Electric Resonators. W. G. Cady. Proc. Inst. Radio Engrs., Vol 12, p. 805 (1924).

(2) Piezo-Electric Crystal Resonators and Crystal Oscillators Applied to the Precision Calibration of Wavemeters. G. W. Pierce. Proc. Am. Acad. of Arts & Sciences, Vol. 59, p. 82 (1923).

Piezo-Electric Crystal Oscillators Applied to the Precision Measurement of the Velocity of Sound in Air and CO_2 at High Frequencies. G. W. Pierce. Proc. Am. Acad. of Arts and Sciences, Vol. 60, p. 271 (1925).

(3) Sichtmachung von hochfrequenten Longitudinalschwingungen pfezo-elek, trischer Kristallstäbe. E. Giebe and A. Scheibe. Zeitschrift für Physik- Vol. 33, p. 335 (1925).

(4) The Structure of α and β Quartz. Sir W. Bragg. Proc. Roy. Soc. A., Vol. 160, No. 751, p. 495 (1925).

(5) Electrically Maintained Vibrations. S. Butterworth. Proc. Phys. Soc., 271, 410 (1915).

(6) A Self-Contained Standard Harmonic Wavemeter. D. W. Dye. Trans. Roy. Soc., Vol. 224, p. 259 (1924).

(7) The Electrical Network Equivalent of a Piezo-Electric Resonator. K. S. Van Dyke. Phys. Rev., Vol. 25, No. 6, Abs. No. 52, p. 895, June (1925).

It has been worked out from first principles that the constants of the network (in terms of the nomenclature used in the present Paper) are as follows :—

$$N=M/4\varepsilon^2b^2,\ K=4\varepsilon^2b^2/g,\ S=N_1/4\varepsilon^2b^2$$

$$\text{and } K_1=\left(\frac{k}{4\pi}-\delta\varepsilon\right)\frac{bl}{e}$$

where M, N_1 and g are the equivalent mass, frictional coefficient and stiffness of control,
δ is the modulus of elasticity, and
ε is the piezo-electric constant in c.g.s. and electro-static units.

(8) New Method of High Frequency Resistance Measurement. E. Mallett and A. D. Blumlein. Inst. El. Eng. J., 63, p. 397 (1925).

Also :—

(9) The Quartz Oscillator. E. Mallett and V. J. Terry. Wireless World and Radio Review, 16, p. 630 (1925).

(10) Piezo-Electrically Induced Vibrations in Quartz Rods. M. v. Laue. Zeitschrift für Physik, Vol. 34, p. 347 (1925).

DISCUSSION.

Dr. Ezer Griffiths : I am interested in the practical applications of the piezo-electric crystal oscillator, as it has great possibilities. When I saw the Paper by Pierce on the precision measurement of the velocity of sound in air and CO_2 at high frequencies it occurred to me that a gas analysis instrument could be based on this principle. Such an instrument would have the advantage of not disturbing the chemical composition of the atmosphere under test. I have made a rough trial of the method for the determination of the percentage of CO_2 in a mixture of air and CO_2, and for this purpose Mr. Dye kindly supplied me with the quartz oscillator shown, which gives out longitudinal waves of frequency about 40,000 per second. The instrument has given promising results. Many other applications can be found for this useful tool, especially in thermal measurements. It is curious to note that piezo-electricity has been known for about 45 years, and that it is only within the last few years that the effect has been turned to practical account.

Dr. D. Owen said that the Paper, like the author's previous contribution dealing with the cathode ray oscillograph, is quite an exceptionally beautiful application of physics and a justification of the phrase " the fairyland of science." He wished Professor Boys, who first discovered the mechanical properties of quartz, could have been present to hear the Paper. The observations relating to the temperature coefficient of natural frequency show that in one case the author can control the frequency to 1 part in 100 million, while the temperature coefficient itself in no case exceeds 1 part in 10,000 per degree. The question as to the cause of the differences in the

temperature coefficients, which the author discusses towards the end of his Paper, offers an attractive field for inquiry.

Mr. R. S. WHIPPLE said that, apart from the great beauty of the scientific work described in the Paper, physicists are much indebted to the author for establishing the extraordinary constancy of Pierce's circuit for maintaining oscillations, which is of the greatest industrial importance.

Dr. E. H. RAYNER said that the author had shown him a crystal sent to the National Physical Laboratory for testing, which had the peculiarity that it exhibited some scores of different natural frequencies, a very striking property in a crystal the size of a sixpence. He also mentioned that the Radio Research Board, at whose instance the work had been undertaken, had adopted the unusual course of releasing the Paper for publication by the Society before they had themselves considered it, on account of its exceptional importance.

The PRESIDENT expressed the thanks of the meeting to the author and to the Radio Research Board.

XXXIX.—THE CURRENT-VOLTAGE CHARACTERISTICS OF ELECTROSTATIC MACHINES WHEN SUPPLYING CURRENT TO NON-INDUCTIVE LOADS AND TO A COOLIDGE X-RAY TUBE.

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SUMMARY.

Experiments are described in which a large electrostatic machine is used as a source of potential for the discharge through (*a*) a Coolidge X-ray tube, and (*b*) a non-inductive resistance. The results are represented in the form of characteristic curves. In the former case it is shown that above a certain critical voltage the discharge is intermittent, while in the latter case the discharge is continuous for all voltages.

The cause of the intermittence of the current through the Coolidge tube is assigned to the operation of the Pearson-Anson effect, and this implies the conclusion that the effect of the residual gas in such tubes is not completely insensible above a certain voltage.

§ 1. *Introduction.*

WHEN an electrostatic machine is driven at constant speed it is generally assumed that it provides a source of constant electromotive force, capable therefore of generating a steady direct current at a constant difference of potential. There appears, however, to be little definite evidence on the question. In Sir J. J. Thomson's "Conduction of Electricity Through Gases" (2nd edition, p. 514) it is stated that a large electrostatic machine gives a continuous discharge, and in proof reference is made to a Paper by Strutt.* Curiously, no mention whatever occurs in this Paper of the use of an electrostatic machine. In a Paper† read before this Society in 1923 an experiment was described, and an actual photograph was shown, from which it was inferred that the current through a Coolidge tube supplied by an electrostatic machine was intermittent. Since the cause of the intermittence might reside in the properties *either* of the Coolidge tube *or* of the electrical machine itself, it was obviously desirable to seek direct evidence as to the constancy of the discharge from an electrical machine when connected to a purely ohmic resistance.

Experiments have been carried out on two large machines, one a 20-plate sectorless machine of the Bonetti type, with ebonite plates 22 in. in diameter ; the other a machine of the Holtz pattern, with 16 movable glass plates 36 in. in diameter. In the first place it was found that when the load is a non-inductive ohmic resistance the current is steady, showing no sign of intermittence at any value of the terminal voltage. This point having been ascertained, it was possible to proceed to the determination of the external characteristic of the machine, expressed as a curve with P.D. across the terminal as ordinate, and the steady load current as abscissa. So far as the author is aware, such characteristics have not been described before. Wommelsdorf‡ has published data respecting electrical machines in the form of curves to which he applied the term *characteristic*, the currents being expressed in terms of the number of sparks per second supplied to a Leyden jar of known capacity.

* Strutt, Phil. Mag., Vol. 48, p. 478 (1899).

† Harlow and Evans, Proc. Phys. Soc., Pt. 4, pp. 9D-25D (1923).

‡ Wommelsdorf, Phys. Zeitschr., December (1904).

Each single observation of this kind involves a series of rises and falls of potential, and it is clear that his curves are in no way comparable with the simple characteristics by which, for example, the action of a direct-current dynamo is usually represented, and which are analogous to those described in the present Paper in relation to the electrostatic machine.

The characteristics obtained are found to consist of two fairly marked stages. As the current gradually increases from zero the curve falls steeply, and is convex towards the origin. A point of inflexion marks this off from the second stage, in which the curve rapidly becomes vertical, so that practically no change of current occurs as the P.D. drops to zero. In the glass plate machine inflexion occurs at a potential of about 45 kilovolts, in the ebonite plate machine at about 20 kilovolts.

Experiments were next made when the load on the machine was a Coolidge X-ray tube. Plotting spark-gap potentials against mean currents, the resulting characteristics were found to differ materially from those found on purely ohmic loads—a fact admitting of only one interpretation, namely, that the current through the Coolidge tube is fluctuating or intermittent. This applies only at the upper voltages, namely, above 35 kv., the currents through the Coolidge tube in this region being distinctly less—down to a half or a third—of the values of the current through a water resistance at the same terminal voltage. Below the critical value of the voltage the characteristics on the Coolidge tube and on the ohmic resistance are indistinguishable.

The probable cause of the intermittence is assigned to the operation of the Pearson-Anson effect. This implies the conclusion that the effect of the residual gas in a Coolidge tube is not insensible above a certain critical voltage, which, it is suggested, is the sparking potential of the gas under the conditions prevailing in the tube.

I. The Characteristic of the Electrostatic Machine on Non-Inductive Loads.

§ 2. *Steadiness of Terminal Voltage.*

In order to solve the problem as to the constancy of the current supplied by an electrostatic machine to a non-inductive ohmic resistance, observations were made with the circuit indicated in Fig. 1. The non-inductive resistances used, represented by R, consisted of water resistances. These were columns of freshly distilled water in glass quill-tubing, a metre or more in length, bent twice at right angles. The tubes, provided with platinum electrodes at various points along their lengths, were first cleansed by successive washings with distilled water, and after a final filling with distilled water the ends were closed with rubber caps. By using a few tubes a sufficient number of resistances were rendered available, covering the range from 100 to 1,000 megohms.

The corresponding range of P.D. across the terminals of the electrostatic machine was 20 to 90 kilovolts. These voltages were measured by the sphere spark-gap, consisting of a pair of polished brass balls SS' 5 cm. in diameter, at a variable and measurable distance apart, a high resistance being placed in series to prevent surges. The values of P.D. in terms of spark length were taken from Kaye and Laby's Tables of Physical Constants.

One terminal A of the machine M was earthed. Currents were measured by a micro-ammeter G inserted in the earthed lead. Various changes were made to

check the possibility of part of the current through G being due to brush discharge, so as to ensure that the current recorded was actually that passing through the resistance R.

The theoretical basis of the measurements is as follows: The spark-gap value gives the peak potential across R, while the micro-ammeter measures the mean value of the current through it. If the quotient of peak potential by mean current agrees with the value of R given by ordinary low-voltage methods, it follows that the current supplied by the machine must be perfectly steady. If, on the contrary, this quotient should exceed the value of R found by the usual steady current methods, the conclusion to be drawn is that the applied voltage, and consequently the current through a non-inductive resistance, is variable or intermittent.

The method used to determine the value of R was to charge a 1/3 microfarad standard condenser to 200 volts, then measure the time of fall to half value when its terminals were connected through the resistance under test. An electrostatic

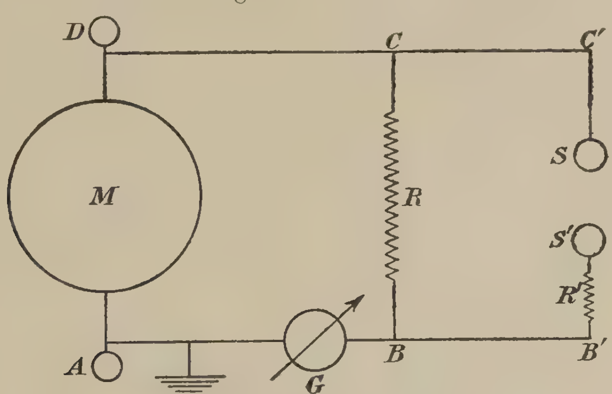

FIG. 1.—CIRCUIT FOR TESTING STEADINESS OF THE CURRENT SUPPLIED BY AN ELECTROSTATIC MACHINE TO A NON-INDUCTIVE OHMIC RESISTANCE.

voltmeter across the condenser indicated the voltages. This measurement was made both before and after an observation with the electrostatic machine.

A representative set of results is shown in Table I. These results show a satis-

TABLE I.—*Test of Invariableness of the Current Supplied by an Electrostatic Machine on Non-inductive Loads.*

Spark Gap (cm.).	Kilovolts (deduced from spark gap).	Mean Current (milliamp.).	$\frac{\text{Kilovolts}}{\text{Milliamp.}} \div 10^6$	R (megohms).	Percentage Difference.
0·625	21	0·195	108	109	−1·0
1·42	42	0·321	130	126·7	+2·5
1·69	49	0·276	177	178	−0·7
1·93	54	0·227	238	237	+0·3
2·15	59	0·110	534	537	−0·6
2·35	63	0·190	331	326	+1·5
2·50	66	0·269	239	238	+0·4
2·76	69	0·188	378	381	−0·8
2·80	70	0·305	236	237	−0·4
2·95	75	0·158	475	474	+0·2
3·56	85	0·121	703	712	−1·3

factory agreement between the quotient of peak volts and mean amperes, and the values of the resistance R. The conclusion is that, over the whole range of voltages used, large electrostatic machines supply a perfectly steady voltage and current to a non-inductive ohmic resistance. An accuracy of 2 to 3 per cent. in the observations was aimed at throughout.

§ 3. *Characteristics on Non-inductive Load.*

The constancy of voltage and current on non-inductive loads being established, it is possible to obtain experimentally the external volt-ampere characteristic of a machine. In conducting the measurements a high-resistance voltmeter V was sometimes substituted for the spark-gap method of measuring potential differences, the connections being as in Fig. 2, in which R denotes the variable part of the load,

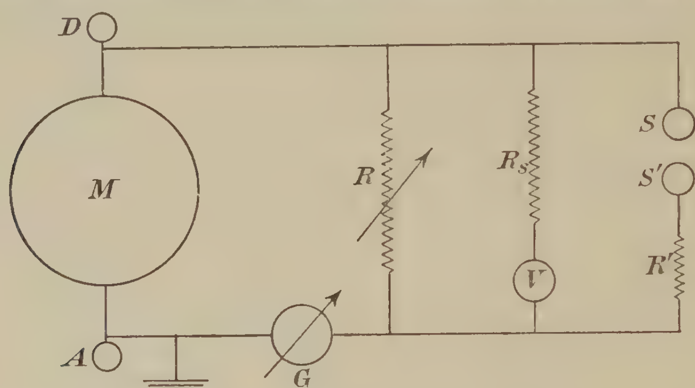

FIG. 2.—CIRCUIT CONNECTIONS WHEN DETERMINING CHARACTERISTIC OF ELECTROSTATIC MACHINE ON NON-INDUCTIVE LOADS.

while R_s is a constant water-resistance in series with a millivoltmeter. The form of the characteristic obtained for a particular machine, depending as it does on atmospheric conditions, is no strictly reproducible curve, but varies from day to day, and even sometimes in the course of a single run. Characteristics obtained at different times agree, however, in general type. Two fair samples, one for the glass plate machine and one for the ebonite plate machine, are shown in Figs. 3 and 4; and the data in one case are shown in Table II.

TABLE II.—*Characteristic of Bonetti Machine.*

Kilovolts.	Milliamps.
66	0·065
58	0·095
40	0·190
30	0·30
25	0·375
16	0·395
10	0·402
0	0·402

These characteristics will be seen to possess the special features already described in the introductory section.

The readings for the lowest voltages were obtained by considerably reducing the external resistance, and finally short-circuiting the terminals of the machine.

When the machine is short-circuited the current gradually dies down to zero. A typical decay curve is shown in Fig. 5.

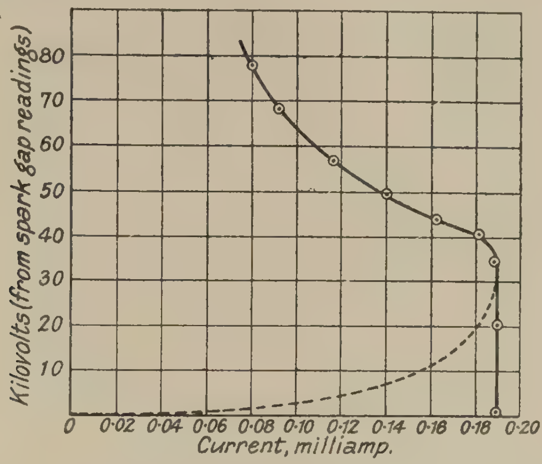

FIG. 3.—CHARACTERISTIC OF ELECTROSTATIC MACHINE (HOLTZ TYPE, 16-PLATE, DIAMETER 36 INS., GLASS) ON NON-INDUCTIVE LOAD.

(The dotted curve suggests the form of the characteristic when traversed infinitely slowly.)

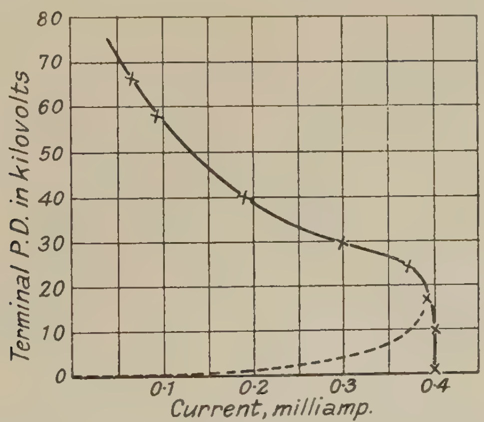

FIG. 4.—CHARACTERISTIC OF ELECTROSTATIC MACHINE (BONETTI TYPE, 20-PLATE, DIAMETER 22 INS., EBONITE) ON NON-INDUCTIVE LOAD.

(The dotted curve suggests the form of the characteristic when traversed infinitely slowly.)

It thus appears that when the terminal voltage becomes very low an electrostatic machine gradually becomes de-excited. In the strictly steady state the characteristics would be probably of the form suggested by the dotted lines of Figs. 3 and 4. They are reminiscent of the external characteristic of a shunt dynamo for very low values of the external resistance.

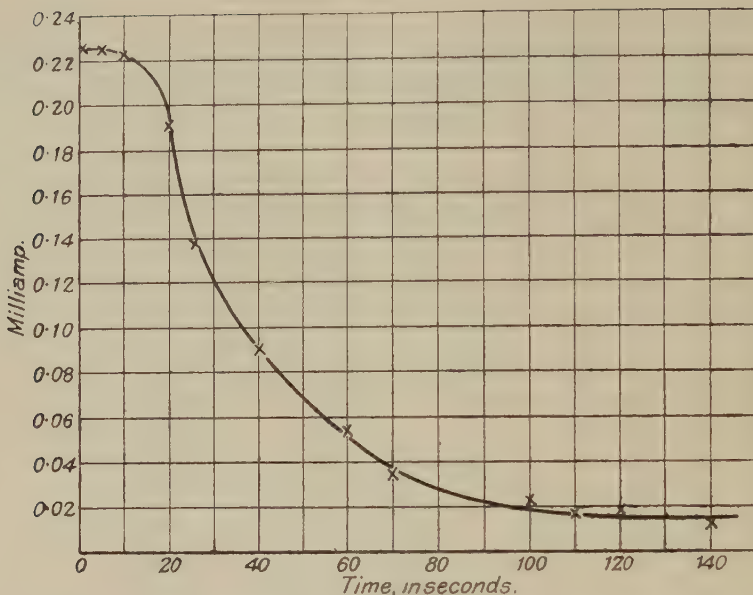

Fig. 5.—Decay of Short-Circuit Current of Electrostatic Machine with Time.

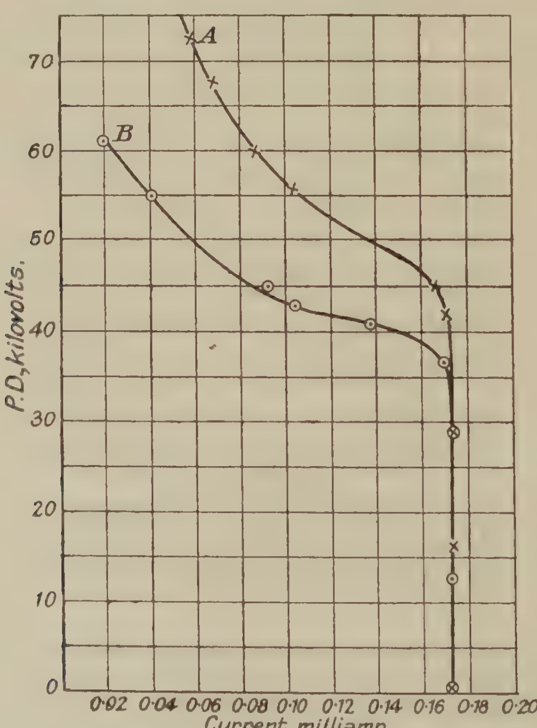

Fig. 6.—Characteristics of Electrostatic Machine.
A. On non-inductive ohmic loads.
B. On Coolidge Tube (for a series of values of filament heating current).

II. Characteristic of an Electrostatic Machine with Coolidge X-Ray Tube as Load.

§ 4.

Observations on the same lines as those above described were made, the Coolidge tube taking the place of the water resistances. The circuit connections were as in Fig. 1, with the difference that the Coolidge tube could be substituted for the water resistances. Voltages were measured by the spark-gap method, and mean current by the moving-coil micro-ammeter.

With the Coolidge tube in circuit, various points on the external characteristic were obtained by using successive values of filament heating current. If the current from cathode to anode of the tube is quite steady, the volt-ampere curve is bound to coincide with the characteristic obtained on ohmic non-inductive load. The curves actually obtained, however, were found to have a special character of their own. In order to eliminate differences arising from accidental variations in the action of the machine, the experimental procedure adopted was to take three characteristics in succession, the first and third in order of time being on water resistances, the middle one on the Coolidge tube. A typical set of observations is given in Fig. 6, the corresponding numerical data being given in Tables III and IV.

Table III.—*Coolidge Tube Loads.*

Kilovolts.	Ammeter Reading.
55	0·041 milliamp.
37	0·173 ,,
61	0·014 ,,
29	0·173 ,,
42·5	0·104 ,,
16·5	0·173 ,,
41	0·138 ,,
43	0·104 ,,
45	0·083 ,,
0	0·173 ,,

Table IV.—*Non-inductive Loads.*

Kilovolts.	Ammeter Reading.
72·5	0·059 milliamp.
60	0·086 ,,
56	0·104 ,,
45	0·166 ,,
42·5	0·173 ,,
68	0·069 ,
18	0·166 ,,
16·5	0·173 ,,
0	0·173 ,,

For the smaller current values the Coolidge characteristic falls definitely below that on non-inductive load. As the current increases the two curves approximate, and the final vertical portions coincide exactly.

The cause of the distinction between the two characteristics cannot remain in doubt. It has been shown in § 1 that on non-inductive ohmic loads both current and voltage are quite steady for any given load. We are therefore led to

the conclusion that at the higher voltages the current taken by the Coolidge tube is fluctuating or intermittent, whilst at the lower voltages the current through the tube is steady. The critical value of the voltage is found to be about 35 kilovolts.

§ 5. *Confirmatory Experiments.*

To confirm the conclusion that for applied voltages exceeding 35 kv. the current supplied by an electrostatic machine to a Coolidge tube is intermittent, the following experiment was made: In parallel with the Coolidge tube was placed a water resistance of value 750 megohms, with a micro-ammeter in series. By varying the filament

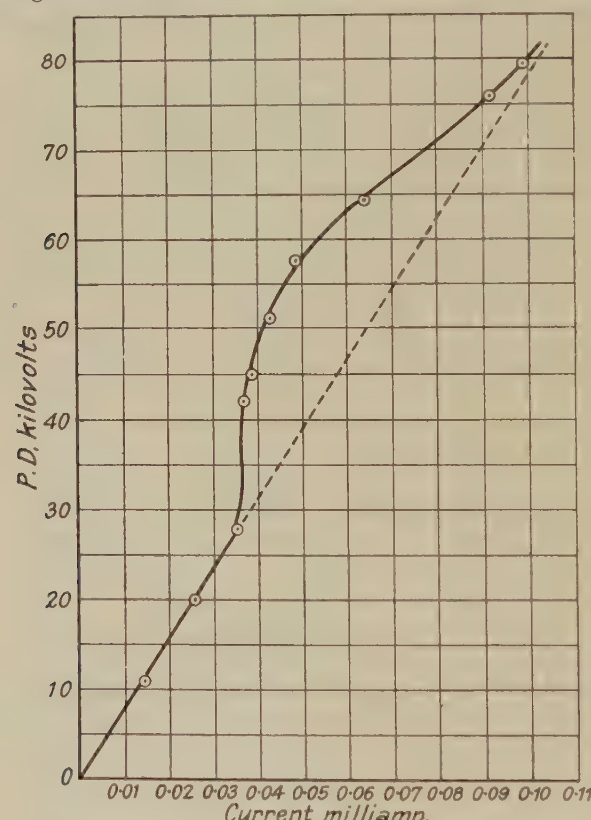

FIG. 7.—VARIATION WITH PEAK VOLTAGE OF THE MEAN CURRENT THROUGH A 750 MEGOHM WATER RESISTANCE PLACED IN PARALLEL WITH A COOLIDGE TUBE ACROSS AN ELECTROSTATIC MACHINE.

current the current through the tube, and accompanying this, the P.D. across the machine terminals was made to vary, so that a set of readings was obtained connecting the mean current through the 750 megohm resistance and the voltage across it as measured by the spark gap. The results are shown in Fig. 7.

It will be seen that below about 35 kv. the observations lie on the straight line, making with the axis of current an angle whose tangent is equal to the resistance of the water tube. Above that critical value of the voltage, however, the current

egins to fall below that corresponding to steady voltages, showing that the current now intermittent. The deviation reaches its greatest value at about 50 kv., the ean current being then less by 33 per cent. than that due to a steady voltage qual to that measured by the spark gap. As the voltage rises still higher the bservations again approach the initial straight line, as is to be expected, since with se of voltage the current through the tube falls, while the current through the fixed esistance rises. Placing a Coolidge tube in parallel with a non-inductive resistance ius causes the current through the latter to become intermittent ; this can only e a consequence of the fact that the current through the Coolidge tube is itself itermittent, it being borne in mind that the electrostatic machine behaves as if possesses a large internal resistance.

Thus the conclusion is confirmed that at a potential difference exceeding a ertain critical value, about 35 kv. for the tube used, the current through a Coolidge ibe is intermittent, while below that value the current through the tube is steady ; ie voltage being in all cases supplied by an electrostatic machine.

Further attempts were made to observe the effects of intermittence by conecting in series with the Coolidge tube a wireless receiving coil of several hundred irns, magnetically coupled to a similar coil in a secondary circuit containing also rectifying crystal and a galvanometer. Preliminary calculation led to the expecition of a just detectable rectified current in the secondary circuit. The effect f the slight sparking at the collectors of the machine tends, however, to mask the esults, and although deflections were obtained they could not be regarded as decisive.

6. *Remarks on the Cause of Intermittence of Current in the Coolidge Tube.*

The existence of intermittence or fluctuation in the passage of electricity irough gases is a phenomenon which has been long recognised. There appears to be everal distinct types of this effect. There is the effect discovered by Whiddington,* here the action is of a simple nature, the fundamental frequency of intermittence eing proportional to the square of the voltage applied to the electrodes, and deterined entirely by the conditions within the tube itself. More recently Appleton nd West† have recorded observations of the phenomenon to which they apply the rm ionic oscillation, associated with the striated discharge ; the effect being here so apparently independent of conditions external to the tube. The most usual iuse of intermittence, however, appears to reside in the Pearson-Anson‡ effect, which the period of intermittence of current through the discharge tube is conolled by resistance and electrostatic capacity external to the tube.

In regard to the effect in the Coolidge tube described in the present Paper, the planation that appears most probable is on the lines of the last-named effect. It volves the assumption that an appreciable, though not large, fraction of the current rough a Coolidge tube is, for voltages exceeding a certain critical value, carried the residual gas in the tube ; the remainder of the current being carried by the ire electronic emission from the cathode. The critical voltage may be identified th the sparking potential of the gas in the tube. The terminal P.D. of an elecostatic machine giving 150 kv. on open circuit appears to drop to half value when

* Whiddington, Radio Review, November (1919).

† Appleton and West, Phil. Mag., May (1923).

‡ Pearson and Anson, Proc. Phys. Soc., Vol. 34, p. 204 (1922).

NN 2

a water resistance of 1,500 megohms is placed in circuit with it. Assuming, then, an effective internal resistance of 1,500 megohms in the machine, and an estimated capacity of $50 \mu\mu F$. due to the machine terminals, Coolidge tube and connections, a period of intermittence of the order of 0·075 second is to be expected—that is, a frequency of about 13 per second. This is of the order of frequency indicated in the photograph recorded by Harlow and Evans (loc. cit.).

This result is apparently in opposition to the usual view that the current through a Coolidge tube is due to the purely electronic emission. It should be noted that the value of the mean current found in the present experiments does not fall below one-half, or at most one-third, of what would be expected if the current were quite steady. In the Paper* in which Coolidge announced the production of his tube it may be pointed out that the very experiments there cited as leading to the conclusion that the discharge is purely electronic point to a systematic drop in the current through the bulb, down to something near half value as the voltage across the tube is *increased*.

It is surely not surprising that the residual gas in a Coolidge tube should make its presence felt to some extent. For, assuming the vacuum to be a few hundredths of a micron (as Coolidge supposes), there would still be some 10^{12} molecules per c.c. left. These molecules are subject not only to the fierce bombardment of the electrons emitted from the hot cathode, but also to the ionising effect of the intense X-radiation in the immediate vicinity of the focal spot on the target. The gas might therefore be expected to take some share in the production of current, this being, of course, necessarily attended by the production of positive ions.

In conclusion, it may be recalled that the results recorded in this Paper also serve to account for the fact that the output of X-rays from a Coolidge tube driven by an electrostatic machine is, if anything, inferior in intensity and hardness to that obtainable when using the rectified voltage from an alternator with step-up transformer, the spark-gap voltage in each case being the same; a result very difficult to reconcile with the assumption that in the former case the voltage remains perfectly steady. The existence of intermittence brings into play a double effect; it reduces the total output of X-radiation, and at the same time degrades the average hardness of the rays produced.

My thanks are due to the Senate of the University of London for grants made from the Dixon Fund; to the Medical Supply Association for their readiness to place electrostatic machines at my disposal; to the Principal and Governors of the Sir John Cass Institute, at the Physics Department of which this work was carried out; and also to Dr. D. Owen for his great interest and valuable advice and help in the work.

DISCUSSION.

Major C. E. S. Phillips said that all who are interested in medical X-ray work would welcome this investigation, because practitioners now aim at constant conditions of voltage, and the subject is therefore of considerable practical importance. A modern outfit for supplying the high voltages employed is expensive and bulky; a less elaborate source, giving an E.M.F. in the neighbourhood of 300,000 volts, is greatly needed, and perhaps the Paper would lead some inventor to produce a satisfactory modification of existing electrostatic machines. It seemed very surprising that a Coolidge tube, whose resistance is constant to 1 per cent. with a transformer, should give rise to intermittent current with a machine. Had the author experimented with different types of tube,

* Coolidge, Phys. Review, Vol.2, pp. 409, 430 (1913).

such as a large-volume deep-therapy tube and a radiator tube? It might even be worth while to study the effect of admitting a little gas.

The PRESIDENT said that he should be sorry to think that all Coolidge tubes were subject to residual gas effects, but he had often suspected these in tubes of the radiator type used by the author.

Mr. R. M. ARCHER (communicated): As one who realises the uphill nature of evening research work I would like to congratulate the author on his producing such an interesting Paper. I have had many chances of seeing his experiments and can support his remarks regarding the difficulty of getting his machines to repeat characteristics consistently. Would it be practicable to enclose them in a kind of greenhouse and to maintain the hygrometric and pressure conditions approximately constant? In any case I think it would be worth while to find the dew-point and to record pressure and temperature.

The water-tube resistances are regarded as non-inductive. But has any capacity effect—due, say, to films of moisture on the outer surface of the glass—been noticed? Has the author thought of using some type of oscillograph in any future work? In view of the importance of the research I think the expense would be justified.

Dr. D. OWEN (communicated): The author has carried out experiments which throw light both on the action of an electrostatic machine of the Wimshurst type, and on the actions within a Coolidge X-ray tube. The experiments with non-inductive ohmic resistances show in a straightforward way that the discharge of a large electrostatic machine on such a load is essentially at steady potential. The characteristics obtained with a Coolidge tube as load show such a marked difference, compared with those on resistances satisfying Ohm's law, that it is difficult to resist the conclusion that the discharge in the former case is no longer continuous.

The author attributes the intermittence or fluctuation to the Pearson-Anson effect. The fact that the present experiments reveal the existence of a critical voltage, and that in previous work a definite frequency of inconsistence of the X-rays was observed on a photographic plate certainly seem to favour this explanation. But on the other hand the Pearson-Anson effect is usually seen in a gas discharge at comparatively high pressure, and the existence of this effect in a highly exhausted tube is quite problematical. It requires a very high resistance in series with the tube, and it is possible that whilst the effect occurs when an electrostatic machine is used as generator it may not do so when an induction coil or transformer is substituted.

If the gas in the Coolidge tube takes part in the discharge, the question of the manner of this arises. Taking the current due to gaseous ionization to be of the order of a milli-ampere, as the recorded observations suggest, then the number of univalent ions flowing per second is 5×10^{15}. If the volume of the tube be taken as a litre, and the gas pressure as 10^{-5} mm., then the total number of molecules of gas present is only $3 \cdot 6 \times 10^{14}$. But it must be remembered at the high voltage present, combined with the low pressure, the velocity acquired even by positive ions is very high, so that a gas molecule may be ionized, take part in the discharge and be liberated again from the cathode very many times in one second. Further, the impacts of these ions on the hot cathode will raise its temperature locally and so enhance the pure electronic discharge. The blackening of the bulb of a Coolidge tube may perhaps be due to slow disintegration of the cathode arising thus. In such ways it is possible to picture the minute amount of residual gas producing sensible effects upon the discharge through the tube.

Author's reply: I have not been able to carry out any work with tubes other than those of the radiator type. I have, however, experimented with two radiator tubes, such as are used in X-ray practice. In all the experiments it was found necessary to keep the filament current at about 70 per cent. of that for which the tubes were rated.

With regard to Mr. Archer's suggestion of a "greenhouse" it may be stated that one of the electrostatic machines used was enclosed in a glass case, the air in which was dried by means of sulphuric acid. Records of hygrometric states of the surrounding air, pressure, etc., were kept in some of the early experiments, but no satisfactory information was obtained.

No capacity effects were noticed with the resistances used. An oscillograph, if a suitable one had been available, would have undoubtedly been of very great advantage.

XL.—THE REFRACTION AND DISPERSION OF GASEOUS CARBON DISULPHIDE.

By H. Lowery, *M.Sc.*, *A.Inst.P.*, *F.R.A.S.*, Lecturer in Physics, Technical College, Bradford.

Received May 20, 1926.

I. Introduction.

THE following values of the refraction and dispersion of gaseous carbon disulphide are as recorded by Dufet,* who summarised the data up to the year 1900. No further determinations seem to have been made since that date.

λ	$(\mu-1)\times 10^6$ at 0°C. and 76 cm.	Observer.
White	1524	Arago†
White	1497	Dulong‡
D	1476	Mascart§
Li	1460	Lorenz‖
D	1480	Lorenz

In view of these incomplete data, it was considered desirable to commence an investigation on the refraction and dispersion of gaseous compounds with measurements on carbon disulphide.

II. Experimental.

For the purpose of this work a Jamin interferometer was mounted.

As source, a "point-o-lite" was employed in conjunction with a Hilger constant deviation spectroscope, in which the eyepiece of the telescope was replaced by a second slit. It was thus possible to obtain light of different wavelengths for the experiments on dispersion.

The light leaving the spectroscope was focussed on the slit of a collimator, which directed parallel light on the first plate of the interferometer. The interference bands were observed through a telescope directed towards the second plate.

The refraction tubes were of glass, about 45 cm. long, provided with optically worked glass ends. They were mounted in a tank which stood on a table between the interferometer plates. Water at a constant temperature of 30°C. surrounded the tubes during the experiments, the temperature being controlled by a thermostat. Precautions were taken to screen the plates of the interferometer from the heat of the tank of warm water.

Whilst measurements were being carried out one of the refraction tubes was kept exhausted of air. The other tube was in communication with a reservoir containing pure liquid carbon disulphide initially cooled by being immersed in a

* Recueil des Données Numériques, Vol. I.
† Mem. Sci., t. II, p. 711, Paris (1859).
‡ Ann. de Ch. et Phys. (2 Ser.), t. XXXI, p. 154 (1826).
§ Comptes Rendus, LXXXVI, p. 321 (1878).
‖ Wied. Ann., XI, p. 70 (1880).

vessel of solid carbon dioxide. It was first exhausted of air, and then carbon disulphide vapour was allowed to pass into it as the temperature of the reservoir gradually rose to about 20°C.

Both refraction tubes were connected to mercury manometers. A density bulb communicated with the carbon disulphide apparatus, and was immersed in the tank with the tubes.

The number of interference bands passing a spider line in the telescope was counted whilst the vapour entered the refraction tube. It was found quite easy to read to one-tenth of a band.

Pure liquid carbon disulphide was supplied by Messrs. Woolley, Sons & Co., Ltd., of Manchester.

III. Results.

Previous observers have frequently pointed out the artificial nature of results of refractivity determinations reduced to N.T.P. conditions in the case of vapours which do not obey the gas laws. It is more satisfactory to consider the refractivity in connexion with the density as has been done, for example, by Le Roux,* Lorenz,† Prytz‡ and Cuthbertson.§

In the present work the refractivity and dispersion have been determined as in the experiments of Cuthbertson, and the results are expressed in connexion with the density determinations.

(*a*) *Refractive Index of Carbon Disulphide Vapour.*

The refractive index of carbon disulphide vapour was determined for the green mercury line (λ 5461) in 10 experiments, in each of which about 200 bands were counted, the difference of pressure between the refraction tubes not exceeding 14 cm. of mercury.

The following values were obtained, reduced so as to show the refractivity of carbon disulphide vapour by the same number of molecules as 1 c.c. of hydrogen contains at N.T.P. :—

$(\mu-1)\times10^6$ 1477, 1481, 1472, 1482, 1472,
1475, 1476, 1480, 1473, 1480

Mean ...... 1477 (λ 5461).

The data employed in obtaining the above reduced values were : C=12·000, H=1·008, S=32·064 and density of hydrogen=0·08985 grams per litre. These give the theoretical density of carbon disulphide vapour as 3·393 grams per litre. The density of carbon disulphide vapour is given in the usual collections of physical tables relative to that of air. From the present experiments, the mean density of carbon disulphide vapour is 3·451 grams per litre, the reduction being effected by the expression

$$d=d_0\cdot\frac{(t+273)}{273}\cdot\frac{760}{p}$$

where d is the reduced density, d_0 the observed density at pressure p mms. of mercury and temperature t°C.

* Ann. de Ch. et Phys. (3 Serie), LXI, p. 385 (1861).

† Wied. Ann., XI, p. 70 (1880).

‡ Wied. Ann., XI, p. 104 (1880).

§ Proc. Roy. Soc., A, Vol. 97, p. 152 (1920), and references.

Merely for the sake of facilitating comparison of the results of the present work with those given above by Mascart and Lorenz, the refractive index of carbon disulphide vapour was determined for sodium light (λ5893) in six experiments with the following results :—

$(\mu-1)\times 10^6$ ...... 1480, 1488, 1485, 1486, 1481, 1482.
Mean ...... 1484 (λ5893).

Note.—These results are *not* reduced by considerations of density, but are the values of the refractive index reduced to N.T.P. conditions by the expression

$$(\mu-1)=\frac{n\lambda}{l}\cdot\frac{760}{p}\cdot\frac{t+273}{273}$$

n being the number of interference bands observed, λ the wavelength of the light, l the length of the refraction tubes, p the pressure difference (in mms.) between the tubes and t the temperature of the carbon disulphide reservoir. The mean value of the refractive index of carbon disulphide vapour for λ5461, similarly reduced to N.T.P. conditions, is

$$(\mu-1)\times 10^6=1503.$$

(*b*) *Dispersion of Carbon Disulphide Vapour.*

The dispersion of carbon disulphide vapour was measured in three sets of double experiments, employing the same dispersion points as in Cuthbertson's work. The results are shown in the following table :—

λ in Å.U.	$(\mu-1)\times 10^6$		Difference.
	Observed.	Calculated.	
Li 6708	1436·4	1436·4	0
Cd 6438	1443·3	1443·1	−2
Hg 5791	1463·2	1463·3	+1
Hg 5770	1464·0	1464·1	+1
Hg 5461	1476·7	1476·8	+1
Ag 5209	1488·8	1489·0	+2
Cd 5086	1495·6	1495·8	+2
Cd 4800	1514·6	1513·9	−7

The values in the second column are those actually obtained in the experiment reduced from density considerations.

Employing the Sellmeier type of dispersion formula, the results are summarised by the expression

$$\mu-1=\frac{5{\cdot}3530\times 10^{27}}{3926{\cdot}6\times 10^{27}-n^2}$$

n being the frequency of the light $=\frac{v}{\lambda}$. v, the velocity of light, is taken as 3×10^{10} cm. per sec.

The values in the third column have been calculated from this expression.

I desire to express my hearty thanks to Professor W. L. Bragg, F.R.S., for suggesting the research, for the loan of apparatus, and for much encouragement ; also to Mr. C. Cuthbertson, F.R.S., for his helpful advice and loan of apparatus ; and to Principal H. Richardson and Mr. J. A. Tomkins, Technical College, Bradford, for their interest in the work.

Fig. 1.

[To face page 473

XLI.—ON THE USE OF INVAR STEEL FOR PRECISION BALANCES.

By J. J. Manley, *M.A.*, Fellow of Magdalen College, Oxford.

Received May 28, 1926.

Abstract.

The Paper deals with certain advantages and disadvantages which accompany the use of invar steel for the beam of a precision balance.

It was found that such a beam exhibits but little in the way of fatigue effects; and also that its sensitivity is nearly the same for all loads.

Experiments prove that the resting-point of the balance notwithstanding the small coefficient of expansion of invar steel, may be appreciably affected by changes in temperature. This is attributed to slight relative movements amongst the several knife-edges and not to a differential lengthening of the beam itself.

The instrument is affected by magnetic storms and also by the diurnal variations in the earth's magnetism. Magnetic effects may, however, be nullified by weighing according to the method of Gauss or by a method of difference.

The conclusion reached is that provided due precautions are observed, invar steel is eminently suitable for the beams of high-grade precision balances.

At the exhibition held by the Physical and Optical Societies in January last, Messrs. L. Oertling showed a newly designed precision balance having a beam of invar steel. This particular use of invar steel is, I believe, an innovation; and as the behaviour of the alloy when used as a beam is of interest not only to chemists, for whom the balance is primarily intended, but also to physicists engaged upon problems involving highly accurate weighing, it seemed desirable that the new balance should be subjected to a series of tests in order that inherent merits and defects might be revealed.

Theoretically, the chief advantages offered by invar steel are high rigidity and a low temperature coefficient. Hence, given a correctly designed beam, the sensitivity will not be affected when the load is changed; neither will the usual small temperature variations within and about the beam, appreciably alter the resting-point R.P. It is true that the known secular changes in the steel will tend to lengthen the beam: such changes are, however, exceedingly small and slow; also in the case of short bars they are probably very uniform; their possible effects are therefore altogether negligible.

In opposition to admitted advantages, we have the changeful influence of the earth's magnetism manifesting itself as fluctuations in the R.P. of the beam; and to these must be added others due to purely local fields. The total effect is therefore ascertainable by direct experiment only.

For an opportunity of carrying out the necessary tests I am indebted to the makers, who, of their own initiative, very kindly offered me the loan of a new balance.

The beam, cut from a plate 2·5 mm. thick and highly polished, has the form shown in Fig. 1. Its length is 15·2 cms. and its depth at the centre 7 cms. The coefficient of expansion of the alloy which contains 36% of nickel, is 87×10^{-8}. The

balance will carry a maximum load of 200 grms., and the sensitivity S as given by the makers, is ·01 mg. There is, however, no difficulty in increasing S to the value of ·003 or even more.

Before experimenting, the balance was cleaned and then placed upon a rigid support. The support consisted of a large earthenware pipe, the lower end of which was embedded in the concrete beneath the floor. To the upper end was cemented the glazed slate required for carrying the instrument. Next, the necessary adjustments were made, and the balance left undisturbed for some days. Experience shows that in this way a balance assumes its most normal condition.

For obtaining the utmost accuracy in weighing, the makers use, in addition to the ordinary scale and pointer, the now well-known device of a plane mirror attached to the beam, and a totally reflecting prism for directing the light incident from a lamp. For all the tests herein recorded, the lamp and its millimetre scale were set up at a distance of 3 ms. from the balance ; the effective pointer of light was therefore 6 ms. long. The examination of the balance was in the main conducted according to methods fully described elsewhere ;* hence much in the way of experimental detail is here omitted.

The balance having acquired a normal state was successively tested for—

α Fatigue effects.
β Changes in sensitivity for various loads.
γ Influence of temperature upon the resting-point R.P.
δ Magnetic effects.
ε Variations due to changes in the earth's magnetism ; and lastly
η The possible effects of convection currents.

α. *Fatigue Effects.*—To discover whether the balance during use became fatigued,† various loads were tried ; these ranged from 0 (empty pans) to the maximum load for which the balance was built. The effect of each load was ascertained only after the beam had been given a lengthy rest. Each experiment was started by releasing the beam, so that the amplitude of its swing approximated to the greatest value indicated by the ivory scale behind the pointer. Observations of the turning-point were commenced after the completion of the first swing, and continued until the amplitude was quite small. In this way data were obtainable for some 12 or 16, or even more, independent and successive calculations of the resting-point R.P. Finally, when the beam no longer vibrated, the actual R.P. was noted and compared with those already deduced. The R.P.'s determined vibrationally were each calculated from groups of three observations of the turning-point. Table I summarizes the results of these experiments.

From Table I it may be seen that, even if the maximum variation in the R.P. for any load be wholly assigned to fatigue effects F, the average error would still not exceed 0·02 mg. Actually, the observed differences are largely due (1) to disturbances set up when the beam is released, and (2) to irregular movements imparted to the unscreened pans by convection currents (vide infra). Hence the conclusion to be drawn from this series of tests is that the rigidity of the beam

* Phil. Trans., A, Vol. 210, pp. 387-415 ; and Proc. Roy. Soc., A, Vol. 86, pp. 591-600.
† Phil. Trans., A, Vol. 210, p. 399.

and its attachments is of the highest order. This is supported by the evidence of the next series, β.

TABLE I.

Sensitivity $S = 146$.

Fatigue, F.	Load.	No. of determinations.	Resting-Point, R.P.				
			Mean.	Max.	Min.	Average diff. from mean value.	R.P. (static).
Mg.	Grms.					Mg.	
0·0308	0	16	302·6	305·3	300·8	$\pm 0{\cdot}4 = \pm 0{\cdot}0027$	302·5
0·0192	10	14	227·6	228·8	226·0	$\pm 0{\cdot}33 = \pm 0{\cdot}0023$	228·5
0·0192	20	16	248·4	249·8	247·0	$\pm 0{\cdot}26 = \pm 0{\cdot}0018$	Not observed
0·0089	50	15	287·2	287·8	286·5	$\pm 0{\cdot}14 = \pm 0{\cdot}0010$	287·0
0·0240	100	13	227·1	228·5	225·0	$\pm 0{\cdot}43 = \pm 0{\cdot}0029$	228·0
0·0137	200	14	243·9	245·3	243·3	$\pm 0{\cdot}20 = \pm 0{\cdot}0014$	242·5
0·0193	=mean.						

The period of 1 vib. varied from 33″-65″.

β. *The Sensitivity S for Different Loads.*—For obtaining definite information concerning the sensitivity S, the position of the gravity bob was adjusted so that S acquired a value approximating 300. S was then determined for a series of loads with the following results :—

TABLE II.

Load.	0	2	4	5	10	20	50	100	200 grms.
S.	274	284	300	305	302	297	306	309	310 per 1 mg.

Neglecting for the moment the values of S for the loads 0 and 2, we note that for all loads of 4 grms. and more the average sensitivity is 304, the mean variation being $\pm 4 = \pm 0{\cdot}013$ mg. With regard to the first and second values, it seems quite clear that as the load is increased from 0 to 4 slight readjustments occur ; and that for all loads ranging from 4 to 200 grms. the relative positions of the beam and its attachments are retained almost rigidly. It may be observed that, for the balance under discussion, S would have been rendered very nearly constant by the simple expedient of increasing the weight of each pan by 4 grms. It is believed that, apart from the values of S for the loads 0 and 2, the deviations from the mean value of 304 are mainly due to the irregularities named in the preceding section α and dealt with in the concluding section η.

γ. *Temperature Effects.*—We know that the R.P. of a balance may vary with the temperature. It is difficult to account for such changes on the assumption that each arm of the beam possesses a distinctly different coefficient of expansion ; and this must be evident when we reflect upon the care exercised in the preparation and selection of the alloy. The variations in the R.P. are, however, readily understood if we grant that a changing temperature brings about small relative movements amongst the several knife-edges. Now, if this view be correct, it will be seen that, even when the material composing the beam possesses a zero coefficient of expansion, it does not follow that the balance will be free from temperature effects, and so retain a constant R.P. value ; hence the necessity for the experiments described below. It was desirable owing to the magnetic nature of the beam that these further

experiments should be carried out rapidly and within a period during which the dipping needle was almost quiescent. As it could not be known when the magnetic elements would be favourable, a day was chosen at random, and by chance it proved eminently suitable (vide infra). The experiments were conducted as follows :—

First, each pan was loaded with 100 grms., the beam released and the small room in which the balance stood cooled down as much as possible overnight. The R.P. and the temperature of the beam case were determined on the following morning. Next, the temperature of the room was slowly and continuously increased and from time to time both the R.P. and the temperature of the beam re-observed. Readings were thus obtained for a range of 6·1° C. They are given in tabulated form below.

TABLE III.

R.P.	214	217	219	220	220	219	216	219	220	223	225	227 mm.
Temp.	13·3	14·0	14·6	15·1	15·5	16·0	16·9	17·5	18·2	18·7	19·0	19·4°C.

Maximum difference in temperature = 6·1°C.
Maximum difference in R.P. = 13.
Mean R.P. = 220.
Mean variation in R.P. per 1°C. = ±2·6 = ±0·008 mg.

All the above R.P. values were measured statically and not as is usual, vibrationally ; in no case was the beam arrested. Thus minute relative displacements

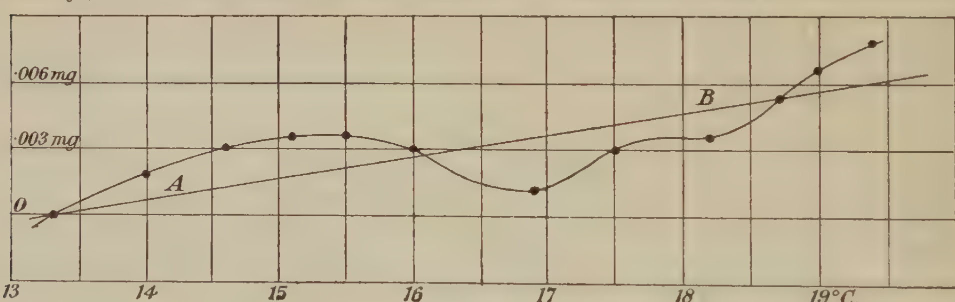

FIG. 2.

of the knife-edges, rendered possible by arresting and releasing the beam, were avoided. It should, however, be noted that the beam was seldom in a state of perfect rest ; generally, the reflected light was moving across the scale to the extent of 1 mm. or 2 mm.

On plotting the R.P.'s against correlated temperatures, as in Fig. 2, we obtain a graph representing positive and negative movements about a mean axis *AB*. The experimental results, therefore, support the suggestion already advanced, namely, that with a varying temperature minute but unequal readjustments occur within the attached knife-edge systems. These readjustments appear to be smooth, but they are not uniform. In some cases the L-arm of the balance is lengthened, but in others the R-arm is similarly affected.

From the data given in Table III we find that the balance exhibited for the limits within which it was tested, a mean temperature coefficient *k* equal to +0·008 mg. per 1°C. It must, however, be observed that *k* would almost certainly

vary with the load; and this because some loads assist the relative movements of the knife-edge blocks to a greater extent than do others. It was possible that the changes in the R.P. tabulated above, were in part due to causes which influence the dipping needle. On this point the Astronomer Royal informed me that during April 24 (when the experiments were made), there were "small movements" of the dipping needle at 9 p.m. and again at 11 p.m. Apart from those the needle was undisturbed. The experiments under consideration were all made between the hours of 10 a.m. and 7.35 p.m.; we, therefore, infer that the difference in the R.P.'s as shown in Table III, were not, to any appreciable extent, due to magnetic disturbances; hence, in the absence of other evidence, the variations in the R.P. are to be regarded as temperature effects only.

δ. The Influence Exerted by a Magnetic Pole.—The effects produced by varying the magnetic field were investigated as follows :—

Two 10 grm. weights, the one gilded and the other platinized, were chosen, and the value of the former measured in terms of the latter. Using the method of Gauss, a first standardisation was carried out under normal conditions; this was followed by three others, during each of which a weak and thin magnet 1 m. long, was given a fixed and vertical position. The additional standardisations were effected with the magnet immediately above (1) the L-pan, (2) the centre of the beam, and (3) the R-pan. In each case the lowest pole was distant from the axis of the beam by 14 cm., and its proximity markedly affected the R.P. *Variations* in the new R.P.'s were not, however, greater than those usually observed. The several values found for the standardised weight were as follows :—

TABLE IV.

Conditions ...	Normal.	Magnet over L-pan.	Magnet over Centre of Beam.	Magnet over R-pan.	Mean.	Difference between Mean and Normal Values.
Weight ...	$9{\cdot}9988_9$	$9{\cdot}9988_8$	$9{\cdot}9988_4$	$9{\cdot}9988_7$	$9{\cdot}9988_6$	$-0{\cdot}00003 = 1$ in 333000

Considering the exceptional character of the tests, the mean of the three standardisations conducted in the presence of the magnet, is in remarkably good agreement with the value obtained under normal conditions. It, therefore, appears that provided the method of Gauss be used and the two weighings effected within the brief period required, the results obtained with an invar steel beam are but rarely influenced by changes in the earth's magnetism, and even then to a small extent only. Attention may now be directed to the diurnal changes observable in the R.P. of the beam.

ε. Variations Due to Changes in the Earth's Magnetism.—During the experimental work of the preceding sections, there occurred on most days, very distinct changes in the R.P. Occasionally such changes were exceedingly well marked even when the beam had been fully fatigued and left unarrested and the temperature maintained nearly constant; they were particularly noticeable on April 13, 14, and 15. Replying to my inquiries, the Astronomer Royal stated that on April 14, at 14 h., G.M.T., a "large" magnetic disturbance began, and lasted for approximately 21 hours. In that period the magnetic inclination varied at least 15′ of arc, this variation being five or six times greater than the normal diurnal range.

By calculation I find that during that same period, the maximum variation in

the angular displacement of the balance beam was 38′; this is 2·5 times greater than the disturbance recorded at Greenwich. Allowance must, however, be made for the fact that the plane of the balance beam intersected that of the magnetic meridian at an angle of about 45°.

The results tabulated below appear to be of interest in that they illustrate still further the effects producible by magnetic disturbances.

TABLE V.

Date.	Max. Variation in R.P.	Equivalent Angular Variation.	Equivalent Variation in Weight.
April 13, 1926	47	27′	0·155 mg.
April 14, 1926	67	38′	0·220 ,,
April 15, 1926	38	22′	0·125 ,,
April 16, 1926	32	18′	0·105 ,,
April 24, 1926	14	8′	0·046 ,,

It now appeared desirable to obtain some direct information from an inclination needle mounted upon the balance bench. Accordingly, the balance was removed, and a needle 6·5 in. long set up in the plane formerly occupied by the beam. The needle rested upon knife edges, and possessed a high sensitivity; its axis carried a small concave mirror so that deflections could be measured optically. The reflected light was caught upon a millimetre scale placed at a distance of about 2·3 ms.; this, under the circumstances, was the greatest obtainable. In the case of the balance, the distance was 3 ms. Hence, if we multiply the deflections of the needle by the ratio 3/2·3, we at once obtain values directly comparable with the similarly produced deflections of the balance beam. The S-seeking pole was loaded, so that the needle when at rest was horizontal. Errors resulting from draughts were excluded by housing the magnetic system within a glass dome. Thus the conditions under which the needle was placed were as nearly as possible identical with those which had obtained for the balance. The preparations having been completed, frequent observations of the needle were made daily from April 27 to May 8, inclusive. The maximum variations noted for each day during this period are, together with certain equivalent values, set forth in the following table :—

TABLE VI.

Date. 1926.	Greatest Variation.	Variations × 3/2·3.	Variations in Angular Measure.	Variations Expressed as Weight Equivalents.
April 27	6 mm.	7·8 mm.	4·4′	0·026 mg.
28	42 ,,	54·3 ,,	31·0′	0·179 ,,
29	2 ,,	2·6 ,,	1·5′	0·009 ,,
30	6 ,,	7·8 ,,	4·4′	0·026 ,,
May 1	3 ,,	3·9 ,,	2·2′	0·013 ,,
3	27 ,,	34·9 ,,	27·0′	0·115 ,,
4	1 ,,	1·3 ,,	0·8′	0·004 ,,
5	3 ,,	3·9 ,,	2·2′	0·013 ,,
6	3 ,,	3·9 ,,	2·2′	0·013 ,,
7	3 ,,	3·9 ,,	2·2′	0·013 ,,
8	2 ,,	2·6 ,,	1·5′	0·009 ,,

It may be noted that during the period of observation the maxima varied within the limits 31′ and 1·5′ of arc, the mean daily variation being 7·2′. Equivalent variations in the R.P. of the balance, correspond to the respective weights of 0·179, 0·009 and 0·038 mg. These are, therefore, the several apparent variations that a mass of 200 grms. or less might have shown had it been frequently weighed in one pan only. This, of course, is an extreme view. Actually, as for example, in the case of a chemical analysis, weights are determined by a method of difference and within a time that is short: and so in the absence of a "great" and rapidly fluctuating magnetic storm, no appreciable error would be introduced. If, however, circumstances as such that two or more required weighings are in point of time, widely separated, the weight sought can still be accurately determined by having recourse to the method of Gauss; and this holds true notwithstanding marked changes in the magnetic field. We may now conclude with a few remarks having a general rather than a restricted interest.

η. *Possible Effects of Convection Currents.*—Elsewhere* I have dwelt upon the importance of shielding the pans of high grade precision balances from draughts. The pans of the balance herein considered, were not specially protected: consequently they were liable to be affected whenever the temperature of the room varied. Changes wrought thus are manifested as the following experiments show, by a definite shift in the R.P.

Exp. 1. The room temperature being almost constant, the R.P. was measured and found to be 321.

Exp. 2. When the beam had come to rest, one hand was held against the right-hand glass panel of the balance case. Within a short time the pointer of light travelled to and fro over 15 scale divisions. The new R.P. was 323.

Exp. 3. The preceding Exp. 2 was tried with the left-hand panel of the case. The pointer vibrated to the extent of 9 scale divisions and the R.P. changed to 319.

The maximum difference produced in the R.P. was 4; and this, as the sensitivity of the balance was 304, was equivalent to 0·013 mg.

Convection currents, generated as in Exps. 2 and 3, may be regarded as light and steady winds moving circularly and in a vertical plane. In Exp. 2 the movement is left-handed and in Exp. 3 right-handed. Winds of this kind will in either case tend to steadily depress one pan and at the same time lift the other; hence a left-handed wind will affect the R.P. positively and a right-handed one negatively. All these disturbances are readily and completely excluded by surrounding each pan and its stirrup with a massive brass cylinder.†

The results obtained may be summarized as follows:—

(1) The rigidity of the beam (apart from the knife-edges) is such that fatigue effects are inappreciable.

(2) As a result of high rigidity, the sensitivity of the balance is nearly the same for all loads.

* Phil. Trans., A, Vol. 212, p. 237.

† Article "Balance," Thorpe's Dict. of Chem. New Edition.

(3) The beam of invar steel like all others examined by the author possesses a distinct though small temperature coefficient, and this in all probability, varies with the load. The temperature coefficient is almost certainly due to relative movements of the several knife edges and not to differential temperature effects in the beam itself.

(4) The beam tends to behave like a dipping needle and is, therefore, influenced by the earth's and local fields ; but during periods of magnetic constancy, the R.P. of the balance remains unchanged. Hence given a non-varying field, accuracy in weighing is in no way disturbed or minimised.

(5) Errors due to variations in the enveloping magnetic field, may be avoided by weighing according to the method of Gauss.

(6) Provided the precautions indicated are observed, invar steel is, in the author's opinion, an eminently suitable material for the beam of a high-grade precision balance.

I conclude by tendering my best thanks to the Astronomer Royal. Upon two occasions I was supplied with data from the Greenwich Observatory, and in this way very materially assisted.

DISCUSSION.

Prof. D. C. MILLER, having been called upon by the President, said that as President of the American Physical Society he welcomed this opportunity of conveying to the Physical Society of London the heartiest good wishes of the members of the American society, who follow with the greatest interest the advances made by British physicists.

Dr. E. H. RAYNER said that he had been reminded by the Paper of an anecdote concerning Mendeleeff, whose influence with the Russian authorities of his day was very great. When the latter wanted scientific information of any kind they applied to Mendeleeff, who sold it at a high price for the benefit of his laboratories. These consequently reached a luxurious level of equipment, and when the Bureau International des Poids et Mesures required a standard metre and kilogramme, the number of significant figures to which the certificate of accuracy was carried did not satisfy Mendeleeff's fastidiousness. Benoît urged, however, that there was in any case no security against some of the microbes on a balance moving along the beam during a measurement, and Mendeleeff was obliged to give way. In the present Paper it would be of advantage if a note on the dimensions of the balance could be added.

Mr. F. A. GOULD (communicated) : The author's experiments on a balance beam constructed of invar steel are interesting inasmuch as a beam of this material has also been in use at the National Physical Laboratory for over two years. Apart from the three knives, which are of agate, and a rigidly-attached lens-mirror used for reading purposes, the invar beam at the N.P.L. is constructed exclusively of invar steel. It was set up with the object of ascertaining whether it gave an appreciably better performance than a gunmetal beam of similar design and dimensions. In the early stages of construction of this beam its linear coefficient of thermal expansion had been determined at the N.P.L. and found to be 0·0000016 per 1° C. between 0° and 30° C. In view of the occurrence of some cases in which certain alloys purporting to be "invar" have been found at the N.P.L. to have a large coefficient of expansion, it would be useful to know whether the author's beam had been definitely proved, by actual determination of its coefficient of expansion, to be of invar steel.

The tests made at the N.P.L. show that, while good performances have been obtained from the invar beam, experiments on chemical balances of the ordinary designs used by English manufacturers do not give sufficiently conclusive evidence as to whether the properties of invar steel render the use of this alloy desirable in the construction of a knife-edge balance of the utmost precision. In spite of the use of invar, the balance beam of this material at the N.P.L. was found to have a temperature coefficient of the same order of magnitude as those of other balances of ordinary construction. A possible explanation of this is indicated in Mr. Manley's Paper.

Mr. R. S. Whipple said that in one of the geodetic surveys a pendulum having rigidly-fixed stellite knife-edges had been employed with success, and in some of the coin-weighing machines used at the Mint the knife-edges actually form part of the beam itself. This feature should be embodied in accurate balances of the future. Possibly a Helmholtz coil would have given a better initation of the earth's field than the means employed by the author.

The author, by way of reply to the discussion, has added at the foot of page 473 some particulars as to the design of the balance.

XLII.—THE SCATTERING POWER OF OXYGEN AND IRON FOR X-RAYS.

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(*Communicated by Prof.* W. L. BRAGG.)

ABSTRACT.

The present Paper describes the results of the quantitative measurement of the intensity of X-ray reflexion from different planes of Fe_3O_4. The side of the unit cell $= 8{\cdot}400$ Å. The parameter, fixing the position of the oxygen atoms, has been determined as $x = 0{\cdot}379 \pm 0{\cdot}001$. F-curves, representing the dependance of the scattering power of oxygen- and iron-ions on the glancing angle, have been obtained. These F-curves (uncorrected for heat-motion) decline much more strongly than the calculated curves for Stoner's distribution of electrons amongst atomic levels.

§ 1.

THE dependance of the scattering power on the glancing angle has first been pointed out by Darwin* and Compton† in theoretical Papers on the intensity of reflexion of X-rays. The first detailed examination of the scattering power of atoms has been made by W. L. Bragg, James and Bosanquet‡ in the case of NaCl. They showed that the scattering power F is not a constant, but dies away rapidly with increasing glancing-angle.

Most of the crystal structures determined up till now have been deduced, assuming the scattering power to be constant and equal to the number of electrons in the atom (or ion). For crystal structures involving many parameters however, allowance for the decline with increasing glancing-angle has to be made.

Some information as to the probable amount of this decline can be gathered from the scattering curves calculated by Hartree.§ As appears from the case of NaCl, the experimental decline is stronger than the calculated one, and it will therefore be necessary to determine the experimental decline for as many atoms as possible.

§ 2.

Fe_3O_4 is a member of the spinel-group of crystals. Its structure has been established by W. H. Bragg|| and S. Nishikawa.¶ The structure is cubic holohedral (space group $O_h{}^7$). The elementary cube, containing eight molecules, is built up of face-centred lattices originating in the following points :—

$$8\,Fe^{++} \qquad 0\,0\,0\,;\ \tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}$$

$$16\,Fe^{+++} \qquad \tfrac{1}{8}\tfrac{1}{8}\tfrac{5}{8};\ \tfrac{3}{8}\tfrac{3}{8}\tfrac{3}{5};\ \tfrac{3}{8}\tfrac{1}{8}\tfrac{7}{8};\ \tfrac{1}{8}\tfrac{3}{8}\tfrac{7}{8}$$

$$32\,O^{--} \qquad x\,x\,x;\ x\,\bar{x}\,\bar{x};\ \bar{x}\,x\,\bar{x};\ \bar{x}\,\bar{x}\,x;$$

$$\tfrac{1}{4}-x,\ \tfrac{1}{4}-x,\ \tfrac{1}{4}-x;\ \tfrac{1}{4}-x,\ x+\tfrac{1}{4},\ x+\tfrac{1}{4};\ x+\tfrac{1}{4},\ \tfrac{1}{4}-x,\ x+\tfrac{1}{4};\ x+\tfrac{1}{4},\ x+\tfrac{1}{4},\ \tfrac{1}{4}-x.$$

* C. G. Darwin, Phil. Mag., 27, 315 (1914).
† A. H. Compton, Phys. Rev., 9, 29 (1917) ; 10, 95 (1917).
‡ W. L. Bragg, James and Bosanquet, Phil. Mag., 44, 433 (1922).
§ D. R. Hartree, Phil. Mag., 50, 289 (1925).
|| W. H. Bragg, Phil. Mag., 30, 305 (1915).
¶ S. Nishikawa, Proc. Tokyo Math. Phys. Soc., 8, 199 (1915).

The side of the unit cell is given by W. H. Bragg as 8·30 Å. A careful determination of the crystal settings for different orders of one plane gave the value 8·400 Å. The value of x has been estimated at about $\frac{3}{8}$, but no accurate determination has been made.

§ 3.

Absolute intensity measurements have been made from (100), (110), (111) and (311) faces. The integrated reflexion was measured in the manner first devised by W. H. Bragg* and described by W. L. Bragg, James and Bosanquet.† In this method the crystal is rotated with uniform velocity through the reflecting angle and the total amount of radiation entering the ionization chamber is measured, allowance being made for general radiation. Each measurement was made in terms of the (400) reflexion of NaCl, for which the absolute intensity was taken as $0{\cdot}94\ 10^{-4}$.‡ The Kα radiation of molybdenum (λ=0·7095 Å) was employed.

TABLE I.

Plane.	Sin θ	$\frac{\varepsilon\omega}{I}10^6$	Structure-amplitude.	S observed.	S calculated.
111	0, 073	8, 1	$8\,Fe^{+++} - 5,66\,Fe^{++} - 5,66\,O\{\cos(45+3\Delta) - \sin(45+3\Delta) - 3\cos(45-\Delta) + 3\sin(45-\Delta)\}$	64	59
220	0, 120	27, 4	$8\,Fe^{++} + 16\,O\{1-\cos 4\Delta\}$	152	153
311	0, 140	52, 5	$8\,Fe^{+++} + 5,66\,Fe^{++} + 5,66\,O\{\cos(45-5\Delta) + 2\cos(45+3\Delta) - \cos(45-\Delta) - \sin(45-5\Delta) - 2\sin(45+3\Delta) + \sin(45+\Delta)\}$	230	230
222	0, 146	13, 8	$16\,Fe^{+++} - 8\,O\{\cos 6\Delta + 3\cos 2\Delta\}$	120	118
400	0, 169	56, 0	$16\,Fe^{+++} - 8\,Fe^{++} + 32\,O\cos 4\Delta$	258	254
333	0, 219	20, 0	$8\,Fe^{+++} + 5,66\,Fe^{++} + 5,66\,O\{\sin(45-9\Delta) - \cos(45-9\Delta) + 3\cos(45+3\Delta) - 3\sin(45+3\Delta)\}$	181	178
440	0, 239	85, 5	$16\,Fe^{+++} + 8\,Fe^{++} + 16\,O\{1+\cos 8\Delta\}$	395	400
622	0, 280	8, 1	$16\,Fe^{+++} - 8\,O\{\cos 10\Delta + 2\cos 6\Delta + \cos 2\Delta\}$	134	130
444	0, 293	11, 0	$16\,Fe^{+++} - 8\,Fe^{++} + 8\,O\{\cos 12\Delta + 3\cos 4\Delta\}$	158	157
800	0, 338	32, 8	$16\,Fe^{+++} + 8\,Fe^{++} + 32\,O\cos 8\Delta$	301	304
660	0, 359	2, 6	$8\,Fe^{++} + 16\,O\{1-\cos 12\Delta\}$	87	87
555	0, 366	6, 7	$8\,Fe^{+++} + 5,66\,Fe^{++} + 5,66\,O\{\sin(45+15\Delta) - \cos(45+15\Delta) - 3\sin(45-5\Delta) + 3\cos(45-5\Delta)\}$	145	147
666	0, 439	4, 3	$16\,Fe^{+++} - 8\,O\{\cos 18\Delta + 3\cos 6\Delta\}$	132	133
880	0, 478	9, 0	$16\,Fe^{+++} + 8\,Fe^{++} + 16\,O\{1+\cos 16\Delta\}$	202	204
777	0, 512	—	$8\,Fe^{+++} - 5,66\,Fe^{++} + 5,66\,O\{\cos(45-21\Delta) - \sin(45-21\Delta) - 3\cos(45+7\Delta) + 3\sin(45+7\Delta)\}$	—	18
888	0, 585	4, 4	$16\,Fe^{+++} + 8\,Fe^{++} + 8\,O\{\cos 24\Delta + 3\cos 8\Delta\}$	162	162

The two crystals used in this investigation showed (100), (110) and (111) faces. Of these, only the latter face was used directly for the intensity measurements. The other faces, being distorted and striated, had to be ground on with emery. Grinding the natural (111) face had no effect on the observed intensities. In

* W. H. Bragg, Phil. Mag., 27, 881 (1914).

† Loc. cit.

‡ From measurements of Wasastjerna.

Table I, column 3, the observed absolute intensities R are given. The accuracy ranges from about 2 per cent. for the stronger reflections to about 5 per cent. for the weakest reflections.

According to Darwin,* the integrated reflection ρ of an ideally imperfect crystal is given by the following expression :—

$$\rho=\frac{\varepsilon\omega}{I}=\frac{4\mu}{N^2\lambda^3}\,\frac{e^4}{m^2c^4}\,\frac{1+\cos^2 2\theta}{\sin 2\theta}S^2e^{-B\sin^2\theta}$$

where N is the number of molecules per c.c. of the crystal, e, m charge and mass of the electron, c the velocity of light, μ the linear absorption coefficient for wave-length λ and including extinction, S the structure-amplitude or number of electrons per molecule efficient in scattering in the direction θ.

The absorption coefficient of Fe_3O_4 has not been determined directly, but can be readily calculated from the values of $\frac{\mu}{S}$ for Fe and O, viz., 36,93 and 1,00 respectively.† From the density of magnetite (5,20) μ is calculated as 141.

Inserting the various numerical values in the above formula, we get :—

$$\rho=\frac{\varepsilon\omega}{I}=1{,}44.\ 10^{-10}\frac{1+\cos^2 2\theta}{\sin 2\theta}S^2$$

in which the heat motion factor is suppressed, so that S really means $Se^{-\frac{B}{2}\sin^2\theta}$ and refers now to eight molecules of Fe_3O_4. From this formula the values of S given in column 5 of Table I are calculated.

In column 4 the structure factors for the different planes are given. As the value of the parameter x differs only slightly from $\frac{3}{8}$, or 135°, this difference $\triangle$ has been used as a new parameter in calculating these structure factors, so that actually $x=135°+\triangle$ when all is expressed in arc measure.

It remains now to determine from these S values, the value of $\triangle$ and the scattering powers of Fe and O.

The iron atoms consist of bivalent and trivalent ones. The nuclear charge for these two kinds of Fe-atoms being the same, the difference in scattering power is only due to a valency electron in the outer layer of the atom. This valency electron, being one of the most loosely bound electrons, will approximately be ineffective as to scattering for larger glancing angles. This fact, that Fe^{++} and Fe^{+++} will be so nearly alike, except for only the very small glancing angles, facilitates the present analysis to a rather large extent.

The value of $\triangle$ being only small, the contribution of oxygen to the structure amplitudes of (220), (311) and (660) may be neglected for a first approximation (*see* Table I). Further, it may be assumed that the scattering power of so light an atom as oxygen has sunk so low for $\sin\theta=0{\cdot}59$ that the (888) reflexion may be regarded as due to iron only. So four points on the Fe-curve have been obtained, by which it is possible to estimate the Fe values for intermediate values of $\sin\theta$. In this way O values can be obtained from the (222), (444), (800) and (666) reflexions,

* C. G. Darwin, Phil. Mag., 43, 800 (1922).

† K. Wingardh, Zeitschr. f. Physik., 8, 363 (1922).

a happy circumstance being the fact that the exact value of $\triangle$ has little or no influence on the magnitude of these structure amplitudes.

A number of considerations lead to the conclusion that extinction in this particular crystal is very small. It is, of course, most important to determine what part extinction plays in reducing the intensities of the reflexions, because the accuracy of the final results for the scattering powers of oxygen and iron depends on the correct estimation of this factor. If extinction is assumed to be negligible, scattering curves for iron and oxygen can be calculated in the way indicated above, using the reflexions (220), (111) and (666) in the case of iron, and thence deducing the oxygen values from (222), (444), (800) and (666). Now it is found that if these values are used to calculate the intensities for reflexions (400) and (440) the results exactly agree with experiment. These are the two most powerful reflexions given by the crystal, so that if extinction existed it would reduce them much more than any others. The fact that this agreement between calculation and observation exists, indicates that the extinction is, at any rate, small compared with the high absorption coefficient, 141, of the crystal.

This argument may be put in another way. If extinction were appreciable, each S value should be multiplied by $\sqrt{\frac{\mu+\varepsilon}{\mu}}$ in order to get the real value. Here the extinction coefficient ε is equal to $\alpha\rho$, in which α is a constant and ρ the integrated reflexion. This correction has been proved to be valid in the case of NaCl, and Darwin has given theoretical evidence for it. The experimental F curves for iron and oxygen are much lower than those calculated by Hartree. We may seek to explain this by supposing that the strong reflexions are reduced by extinction, and obtain an estimate of the extinction coefficient α by giving it a value which raises the reflexion (440) to that to be expected from Hartree's curves. This involves an increase in the value of F for iron to 17·5 instead of 14. The value of α got in this way is not very large, and the only other S values appreciably increased are those for (311) and (400). The estimated value of the parameter is not altered appreciably. If all the results are interpreted with this estimate of extinction, three points on the curves are raised, whereas the remainder remain where they were. It is obvious from the figure that the F values will now lie on a very irregular curve, so that we are forced to abandon this explanation. We may sum up by saying that everything points to a negligible value of the extinction coefficient.

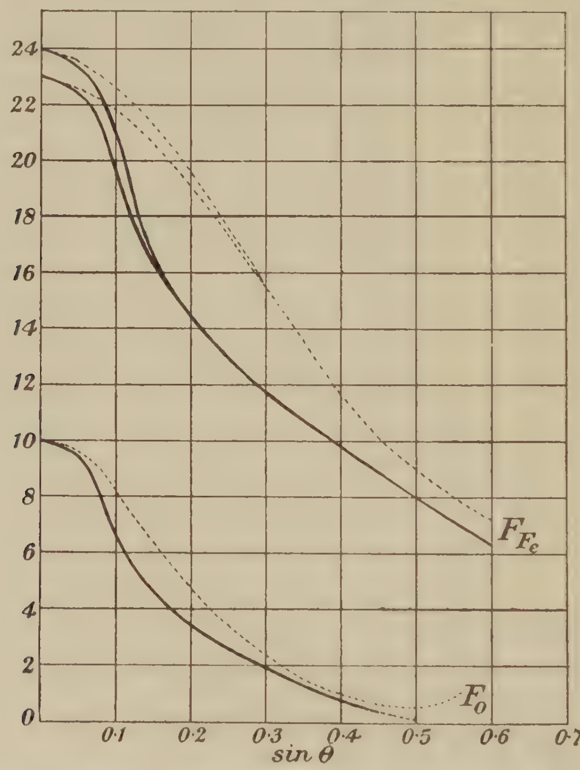
An estimate of $\triangle$ can be made by considering the (111) and (555) reflexions. The structure factor of (555) is very sensitive to small changes in $\triangle$. For $\triangle=0°$ the coefficient in the brackets in Table I is zero; for $\triangle=1°$, 0·7; for $\triangle=1{\cdot}5°$, 1·1; and for $\triangle=2°$, 1·5. Considering the Fe-curve, it follows that S is nearly due to iron only, and that the value of $\triangle$ may not exceed 1·5°. Considering the (333) reflexion, this same limit is found. On the other hand, extrapolating the O- and Fe-curves to $\sin\theta=0$ (ionisation being assumed), it is found that the Fe contribution to (111) amounts to about 50, so that the oxygen contribution is about 14 (which implies that $\triangle$ is positive, as used in the above). Taking the value of $\triangle=1{\cdot}5°$, found above to be the largest one possible, the factor in the brackets becomes 0·25, thus giving a value of about 10 for oxygen. The minimum value of the factor is 0·20. Owing, however, to the exact course of the F-curves for $\sin\theta<0{\cdot}1$ being uncertain, no exacter value for $\triangle$ can be obtained. Thus $\triangle$ is fixed at $136{\cdot}5°\pm0{\cdot}4°$, giving

$x=0{\cdot}379\pm0{\cdot}001$. For $x=0{\cdot}3750$ the oxygen atoms are exactly in cubic close-packing. In column 6 of Table I the calculated values of F from the smoothed F curves are given, using the above value of x. The agreement is very good.

Table II gives the interpolated values of F_0 and F_{Fe} for rational values of sin θ.

TABLE II.

Sin θ	0	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50	0·55	0·60
F	24	23·3	20·9	16·5	14·4	12·8	11·7	10·8	9·9	8·9	8·1	7·2	6·3
	23	22·3	19·8										
	10	9·3	6·8	4·6	3·4	2·6	1·9	1·3	0·8	0·3	0·15	...	...



In the figure the dotted lines represent the calculated F curves. The curve for oxygen was calculated by Hartree. The curve for iron was calculated from Hartree's tables. Both curves are based on Stoner's distribution of electrons amongst atomic levels.

It is seen that in both cases the decline is much stronger than the calculated one. For oxygen this has already been made probable by the work of Bradley* and James and Wood.† As in the case of NaCl, probably only part of this can be ascribed to the heat-motion-factor (the curves being really $Fe^{-\frac{B}{2}\sin^2\theta}$ curves). For

* A. J. Bradley, Phil. Mag., 49, 1225 (1925).
† R. W. James and W. A. Wood, Proc. Roy. Soc., 109, 598 (1925).

large glancing angles the difference becomes much smaller. The rising up again of the oxygen curve for sin $\theta > 0{\cdot}45$, as Hartree's calculated curve does, does not seem to take place ; otherwise the (888) reflexions would have been observed much stronger. It will be very interesting to see in how far this oxygen curve agrees with the oxygen curve determined from other crystals.

I am indebted very much to Professor W. L. Bragg, F.R.S., for his kind help and advice and for suggesting this investigation to me.

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